ISSN: 0128 - 7680

Pertanika Journal of SCIENCE & TECHNOLOGY

VOLUME 2 NO. 2
JULY 1994

A scientific journal published by Universiti Pertanian Malaysia Press

Pertanika Journal of Science and Technology

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Published by Universiti Pertanian Malaysia Press
ISSN No: 0128-7680
Printed by: Ampang Press Sdn. Bhd.

Pertanika Journal of Science and Technology

Volume 2 No. 2 July 1994

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Communication

ISSN: 0128-7680
Pertanika J. Sci. & Technol. 2(2): 121-136 (1994)

A Technique for Transforming Rules in Deductive Databases

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Received 15 December 1992

ABSTRAK

Di dalam pangkalan data deduktif, kecekapan penilaian pertanyaan rekursif dianggap sebagai satu matlamat penting. Suatu pendekatan untuk mencapai matlamat ini ialah dengan menggunakan kaedah-kaedah yang menjelmakan penanyaan asal kepada suatu set pertanyaan baru. Satu dari kaedah-kaedah tersebut ialah "Set Magik". Dalam kaedah "Set Magik", pertanyaan yang diungkapkan oleh petua dijelmakan kepada suatu set petua yang dipanggil petua "magik". Kertas ini menunjukkan cara untuk melakukan penjelmaan tersebut dengan menggunakan struktur data graf petua/matlamat. Kelebihan teknik yang digunakan di sini ialah ianya sangat mudah dan jelas.

ABSTRACT

In deductive databases the efficiency of recursive query evaluation is considered as an important goal. One approach to achieving this goal is to use methods that transform the original query into a new set of queries. One such method is magic sets. In the magic sets method, a query expressed by rules is transformed into a set of rules called magic rules. This paper shows how to perform this transformation by using a rule/goal graph data structure. The advantage of the technique used here is that it is very simple and clear.

Keywords: deductive databases, recursive rules, magic sets, rule/goal graph, logic, query

INTRODUCTION

The integration of logic programming and relational database technologies has resulted in a new model for databases called deductive databases. A deductive database consists of facts and rules and from the syntax point of view it is simply a Prolog program. It is claimed that deductive databases can overcome some limitations of relational databases such as recursion.

Deductive database systems extend relational database management systems, in particular, by allowing recursively defined queries to be expressed as logical rules. Rules (clauses) are usually written in the form of

$$A \leftarrow B_1, B_2, \ldots, B_m$$

where A, B_1, ..., B_m are atomic formulas, and $m \geq 0$. Rules of this type are called Horn clauses and the form in which they are written is known as a clausal form. A rule has both a declarative and a procedural (or problem solving) reading. The declarative reading of the above rule is that for all values of the variables in the rule, A is true, if B_1 and B_2 and ... and B_m are true. The procedural reading is that for all values of the variables in the rule, to solve A, B_1 and B_2... and B_m have to be solved.

Suppose we have a relation (or predicate) *manages* (E, M), which means an employee E is managed by a manager M. Let us define another predicate head (E, H). The intention of this predicate is that H is E's manager, or his/her manager's manager, and so on. Relation head can be expressed by rules as follows:

$$r1 : head(E, M) \leftarrow manages(E, M)$$
$$r2 : head(E, M) \leftarrow manages(E, P), head(P, M)$$

Suppose that we are given the query that asks all the managers of *ahmad.* With respect to the above rules, this query can how be expressed easily as

?head(ahmad, X)

So, a crucial point is to provide efficient methods for handling recursive queries.

A procedure that answers queries on deductive databases must have several important properties. First, it must return all the answers to a query and then stop. These two properties are known as completeness and termination, respectively. Second, the procedure must be efficient, i.e. it must be able to use only necessary (relevant) facts during a query evaluation. Another property is the complexity of the algorithm. While the procedure is able to restrict the computation to the relevant facts, this restriction should not lead to the more expensive procedure, for instance with an exponential cost.

In the past ten years, various strategies have been proposed to handle recursion in logic queries (Reither 1978; Chang 1981; McKay and Shapiro 1981; Henschen and Naqvi 1984; Ullman 1985; Kifer and Lozinskii 1986; Vieille 1986; Beeri and Ramakrishnan 1987). An excellent survey of the methods can be found in Bancilhon and Ramakrishnan (1986). In general, these methods may be classified in two classes, top-down methods and bottom-up methods. Top-down methods, based in proof theory, start with a query as the top goal and generate a proof tree using the axioms (rules) of the database and an inference rule such as resolution to prove that the query is a logical consequence of the database. Prolog is one such system that uses resolution as an inference rule. These methods have proved to be efficient. However, they suffer from a number of problems, including infinite looping, possible non-termination, and they tend to generate answers to queries a tuple at a time. On the other hand, bottom-up methods, based on model theory and fixed point semantics, generate all solutions to a query and do not go into an infinite loop. However, they tend to be inefficient. The reason is that bottom-up methods do not make use of ground terms (variable free terms) in the query in the same way that top-down methods do. As a consequence, many irrelevant tuples are generated during a computation. Techniques are thus needed to restrict the generation of irrelevant tuples.

There are two basic approaches which have been pursued to obtain a more direct computation. The first approach seeks to modify the standard bottom-up computation and achieve a more run-oriented solution (Kifer and Lozinskii 1986; Vieille 1986). The second approach seeks to perform a compile-time transformation of the database, based on the given query, into an equivalent form which enables a standard bottom-up computation to focus on relevant tuples. One example of this approach is the magic sets method (Bancilhon *et al.* 1986).

The magic sets method is an algorithm for rewriting logical rules so as to cut down the number of irrelevant facts during bottom-up evaluation. Special sets of values (tuples), called magic sets, are computed so thay they can be used to restrict the computation to the relevant facts only. These sets are determined by propagating bindings in the query top-down evaluation. Thus, in the magic sets method one can find the positive features of both top-down and bottom-up computation.

The magic sets method consists of the following steps:

i) an analysis of the binding propagation behaviour during the top-down phase,
ii) the generation of magic rules from the original one by using the results obtained from (i), and
iii) the execution of magic rules.

The analysis of the binding propagation can be accomplished by using a tool called a rule/goal (Ullman 1985). In this paper we show how to generate magic rules by using the rule/goal graph. The technique is very simple and clear. The transformation algorithm which produces the same magic rules as our technique was given in Ullman (1989), but that algorithm did not make use of the rule/goal graph. These are other algorithms, such as the one in Sacca and Zaniolo (1987), which result in equivalent magic rules but those algorithms are not very clear.

CONCEPT AND TERMINOLOGY

A deductive database (DDB) D consists of facts (extensional axioms), deductive rules (intensional axioms), integrity constraints, and queries. We use Prolog-like notation for the representation of DDB.

A literal is an atomic formula or the negation of an atomic formula. An atomic formula has the form $p(t_1,\ldots, t_n)$ where p is a predicate symbol of arity n, and each t_i is either a constant, a variable or a function. The atomic formula $p(t_1,\ldots, t_n)$ represents a relation between terms $t_1,\ldots, t_n$.

A clause is a disjunction of literals which has the form

$$A_1 \vee \ldots \vee A_n \vee \sim B_1 \vee \ldots \vee \sim B_m$$

where each A_i and B_j represent an atomic formula. (The symbols, $\vee$, $\wedge$, and ~ denote *or, and, and not* respectively). Clauses can be written in an equivalent form using implication, and in the Prolog style we have

$$A_1 \vee \ldots \vee A_n \leftarrow B_1 \wedge \ldots \wedge B_m$$

All variables in a clause are assumed to be universally quantified. Such a clause is also called a deductive rule, the head of the rule is $A_1 \vee \ldots \vee A_n$, and the body of the rule is $B_1 \wedge \ldots \wedge B_m$. A Horn clause is a clause where the head of the rule is restricted to at most one positive literal.

In this paper we are concerned with a DDB as a set of definite Horn clauses, that is there is no negative literal in the body of deductive rules. Furthermore, literals have no functions. This class of deductive databases is known as a datalog database. A goal clause has a null head, and a clause with a null body is an assertion. An assertion is also called a unit clause. A unit clause which contains only ground terms (variable free terms) is called a ground unit clause or fact. A query is a goal clause.

A clause is called recursive if the same predicate symbol appears in both the head and the body. A relation R may be defined recursively by a recursive clause or by mutual recursion where R is defined (in the head) in terms of S in the body, and in turn S itself is defined in terms of R.

Integrity constraints, expressed as rules, represent restrictions that the database must satisfy, play an important role in checking update validity. They are, however, not needed in answering queries over the database.

Certain predicates are defined by the rules, that is they appear as the head of one or more rules; these are called IDB (intensional database) predicates. Other predicates are not defined by rules, but by a stored relation, and they are called EDB (extensional database) predicates. An EDB predicate can only appear in subgoals; an IDB predicate can appear in both heads and subgoals. We assume that IDB and EDB are mutually exclusive.

RULE/GOAL GRAPH

Before going further, it is convenient to introduce the concept of sideways information passing (Beeri and Ramakrishnan 1987). Informally, a sideways information passing describes how bindings (constants assigned to variables) passed to a rule's head are used to evaluate the predicates in the rule's body. When a sideways information passing is performed, it appears that starting from a predicate name with variables bound in certain positions, we reach the same predicate name with variables bound in other positions. It is thus necessary to distinguish which argument is bound and which is free in a predicate. This leads to the concept of adornment (Ullman 1985).

An adornment or a binding pattern for an n-ary predicate p is a string s of length n of b's and f's, where b stands for bound and f stands for free. The adornment indicates which arguments of p are bound and which are not. If the ith symbol of the adornment is b, then the ith argument if p is bound. If the ith symbol of the adornment is f, then the ith argument of p is free. For a predicate p with an adornment s, we write p^s to denote the adorned predicate for p.

A rule adornment indicates which variables are bound at a point and which are free. The algorithm to decide when a variable becomes bound in a rule

$$H \leftarrow G_1,\ldots,G_k$$

follows from the sideways information passing described earlier.

1. A variable appearing in a bound argument of the rule head is bound before processing any subgoals.
2. A variable is bound after processing subgoal G_i if it was bound before processing G_i or if it appears anywhere in G_i. A rule adornment is denoted by a superscript of the form $[X_1,\ldots, X_m | Y_1, \ldots, Y_n]$, where the X's are bound and the Y's are free. We write $r_{i,j}^{[A|B]}$ to denote that [A|B] is a rule adornment for rule r_i after the consideration of the jth subgoal of r_i.

The binding patterns of predicates in a set of rules and a query can be represented by a finite structure called a rule/goal graph. The concept of a rule/goal graph originally appeared in Ullman (1985) and the rule/goal graph we used follows the one found in Ullman (1989). The rule/goal graph has two types of nodes, namely rule nodes and goal nodes. Goal nodes represent rule adornments.

Let p be the predicate of the query and a be the adornment of that predicate. The process of creating the rule/goal graph starts with the node p^{α}. From this node, we expand the graph according to the rules given below. As we expand, we add goal nodes and rule nodes. For rule r_s, we use $r_{s,0}$, with an adornment, to represent rule r_s before considering any subgoals, and $r_{s,i}$, with an adornment, to represent rule r_s after considering its first i subgoals. The steps to expand the rule/goal graph are as follows (Ullman 1989):

1. A goal node with an EDB predicate has no successors.
2. A goal node that is an IDB predicate p with an adornment a has successors corresponding to all the rules with head predicate p. If r_s is such a rule, then p^{α} has successor

   $$r_{s.0}^{[X_1, \ldots, X_n | Y_1, \ldots, Y_m]}$$

   where $X_1, \ldots, X_n$ are all the variables that appear in a argument of r_s's head that is bound according to adornment a, and $Y_1, \ldots, Y_m$ are the other variables of r_s.
3. Consider a rule node $r_{s.i}^{[X_1, \ldots, X_n | Y_1, \ldots, Y_m]}$, $i \geq 0$, and suppose $q(t_1, \ldots, t_k)$ is the i + 1st subgoal of r_s.

   a) One successor of this rule node is a goal node q^p; p is the adornment that makes the jth argument of qbound if all variables appearing in t_j are among the bound variables of the rule so far. Adornment p makes the jth argument free otherwise.

   b) If i + 1 is less than the number of subgoals in rule r_s (i.e. $q(t_1, \ldots, t_k)$ is not the last subgoal of r_s), then node

   $$r_{s.i}^{[X_1, \ldots, X_n | Y_1, \ldots, Y_m]}$$

   has a second successor, the node

   $$r_{s,i+1}^{[X_1, \ldots, X_n, U_1, \ldots, U_j | V_1, \ldots, V_h]}$$

   where $U_1, \ldots, U_j$ are those variables among $Y_1, \ldots, Y_m$ that appear in $q(t_1, \ldots, t_k)$, and $V_1, \ldots, V_h$ are the remaining variables of the Y's.

Let us consider the same generation rules of *Fig. 1*.

r0 : sg (X, X) ← person (X).

r1 : sg (X, Y) ← par (X, XP), sg (XP, YP), (Y, YP).

Fig. 1. Rules for the same generation

Predicates *person* and *par* are EDB predicates and predicate sg is the only IDB predicate. The intention of predicate *person* (X) is that an individual X is a person. *Par* (X, Y) means Y is the parent of X. The intended meaning of sg (X, Y) is that X and Y are of the same generation. Rule r0 says that every person is of the same generation as her/himself. Rule r1 says that two individuals are of the same generation if their parents are.

Suppose the query is of the form sg^{bf}, that is, given an individual a find all persons who are of the same generation as a. The rule/goal graph constructed by using this query and following the given order of subgoals in the second rule is shown in *Fig. 2.*

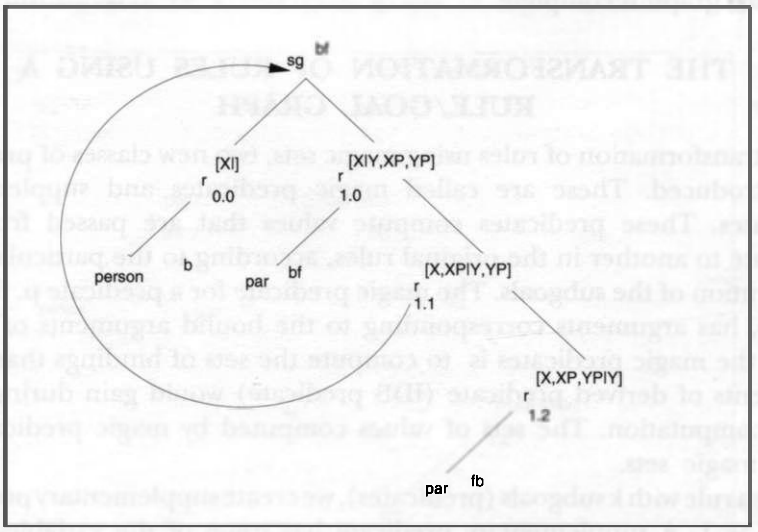

Fig. 2. The rule/goal graph for the same-generation rules

The root has adorned predicate sg^{bf}, which is the predicate in the query with its adornment. The root has two children corresponding to two rules for sg. For each child, the binding on the first argument of sg provides a binding for variable X only. The binding on variable X in rule r_0 causes the argument of the subgoal *person* (X) abound, as shown by the goal node $person^b$, the child node of $r^{[X|]}_{0.0}$.

The other child of the root is

$$r^{[X|Y, XP, YP]}_{1.0}$$

This node has child par^{bf}, representing the first subgoal of r_1. The adornment is bf, because the binding on X provides a binding for the first argument of *par* (X, XP), but not for the second. The other child that the node has is

$$r^{[X, XP|Y, YP]}_{1.1}$$

for which the variable XP becomes bound after considering the first subgoal. This node in turn has two children sg^{bf} and

$$r^{[X, XP, YP|Y]}_{1.2}$$

The former is the same as the root node, thus a new node is not needed. The latter has one and only child *par*^{fb}, representing the last subgoal of r_1, namely *par*(Y, YP). The first argument of this subgoal is free, while the second one is bound. Since no more nodes can be added, the construction of the rule/goal graph is complete.

THE TRANSFORMATION OF RULES USING A RULE/GOAL GRAPH

In the transformation of rules using magic sets, two new classes of predicates are introduced. These are called magic predicates and supplementary predicates. These predicates compute values that are passed from one predicate to another in the original rules, according to the particular order of execution of the subgoals. The magic predicate for a predicate p, denoted by m.p, has arguments corresponding to the bound arguments of p. The aim of the magic predicates is to compute the sets of bindings that bound arguments of derived predicate (IDB predicate) would gain during a top-down computation. The sets of values computed by magic predicates are called magic sets.

For a rule with k subgoals (predicates), we create supplementary predicates S_0,..., $S_k - 1$. A supplementary predicate has some of the variables of the rule as its arguments. For instance, S_i has arguments corresponding to those variables that are both bound and relevant after considering the first i subgoals. Variables are bound either by appearing in a bound argument of the head or by appearing in one of the first i subgoals. Variables are relevant if they appear either in the head or in the (i + 1)st or a subsequent subgoal. The supplementary predicate S_i is used to pass the bindings obtained so far, to the (i + 1)st subgoal.

Magic rules resulting from the magic sets algorithm of Ullman (1989) can be classified into five groups:

i) Rules for the magic predicates,
ii) Rules for the zeroth supplementary predicates,
iii) Rules for the other supplementary predicates,
iv) Rules for IDB predicates, and
v) The initialisation rule.

We now describe how to generate the above rules by using a rule/goal graph.

A rule/graph can be seen as a tree if we omit all arcs linking rule nodes with goal nodes which appear before the rule nodes, during the construction of the rule/goal graph. A tree can be traversed without going into an infinite loop. We want to show that by visiting each node of the tree using a depth-first search, we can generate all magic rules. Our first task is to remove all the arcs in the rule/goal graph that give rise to loops.

Suppose there is a link between rule node P and goal node Q that appears at a level higher than the level of P. To remove this link, we create a new goal node, say Q′, with the same adorned predicate as Q, and make Q′ a child node to P. Node Q′ does not have any successors. The corresponding tree of a rule/goal graph of *Fig.2* is shown in *Fig.3*.

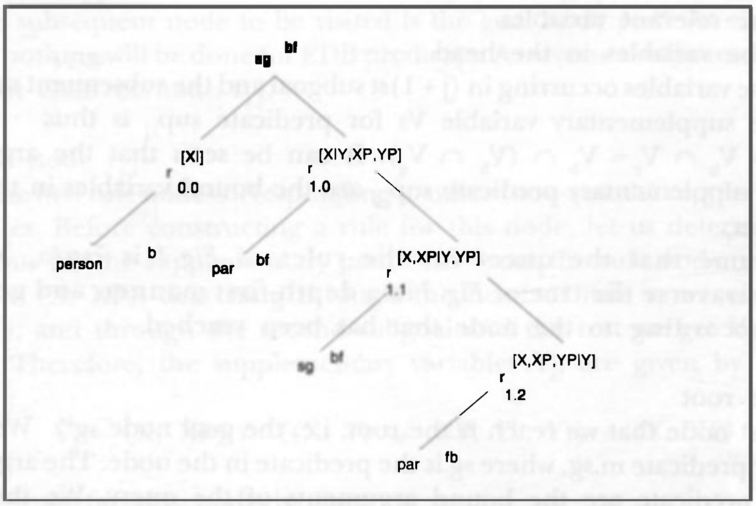

Fig.3. Rule/goal graph for the same-generation rules with the loop removed

In the following, when we refer to a tree we mean a rule/goal graph which has been transformed into a tree.

The next step is to traverse the tree starting from the root. The root is the node which was first created. As we traverse the tree, each time we reach a node, rules will be generated according to that node. For our purpose, nodes of the tree can also be classified into five groups, each of which is associated with a particular type of rule as follows:

a) The root – the initialisation rule,
b) Goal nodes with IDB predicates – rules for magic predicates,
c) Rule nodes $r_{i,0}$ – rules for zero supplementary predicates,
d) Rule nodes r_{ij} where j ≠ 0 – rules for other supplementary predicates, and
e) Rule nodes with only one successor, i.e. their goal-node child – rules for IDB predicates.

These groups are not necessarily disjoint groups. A node might belong to more than one group. For example, node $r_{0.0}$ of *Fig.3* belongs to group c and e. Before we go further, let us see how we can determine the arguments for the supplementary predicates.

A supplementary predicate associated to jth subgoal of rule r_i is denoted by supi.j. The arguments of supi.j are variables of rule r_i that are both bound and relevant after considering the first j subgoals. Recall that variables are bound either by appearing in a bound argument of the head or by appearing in one of the first j subgoals. Variables are relevant if they appear either in the head or in the (j + 1)st or a subsequent subgoal.

Let

V_b be a set of bound variables after considering the first j subgoals

V_r be relevant variables

V_h be variables in the head

V_q be variables occurring in (j + 1)st subgoal and the subsequent subgoals.

The supplementary variable Vs for predicate $sup_{i,j}$ is thus $V_s = V_b \cap V_r = V_b \cap (V_h \cap V_q)$. It can be seen that the arguments for the supplementary predicate $sup_{i,0}$ are the bound variables in the head of rule r_i.

Assume that the query for the rules of *Fig. 1* is ?sg(a, X). Let us now traverse the tree of *Fig. 3* in a depth-first manner, and generate rules according to the node that has been reached.

1. The root

The first node that we reach is the root, i.e. the goal node sg^{bf}. We create a magic predicate m.sg, where sg is the predicate in the node. The arguments of the predicate are the bound arguments of the query. We thus have the initialisation rule

m.sg(a).

2. Rule node $r_{0,0}$

We create the rule for zeroth supplementary predicate sup0.0. The arguments of this predicate are bound variables of the node, that is X. The body of the rule is m.sg(X), where sg is the head predicate of r_0 and X is the bound arguments of the head. We thus have rule

sup0.0(X) ← m.sg(X).

The next node to be visited is the goal node *person*^{b}. Because it contains EDB predicate, no rules are created for this node. We then go back to the node $r_{0,0}$ and look for the right node. It happens that no such node exists, and so we create one of the rules for IDB predicates:

sg(X,X) ← sup0.0(X), person(X).

The head of the resulting rule is the head of rule r0. The first subgoal in the body is the supplementary predicate corresponding to the current node, and the second subgoal is the last subgoal of rule r_0.

We have finished visiting one branch of the root node. We next traverse the right branch of the root.

3. Rule node $r_{1,0}$

The way we create the zeroth supplementary rule for this node is the same as for rule node $r_{0,0}$. But here the rule involved is r_1. Thus,

$$\text{sup}1.0(X) \leftarrow \text{m.sg}(X)$$

The subsequent node to be visited is the goal node par^{bf}. As explained before, nothing will be done for EDB predicate. A traverse continues through the right child of node $r_{1,0}$.

4. Rule node $r_{1,1}$

This is the first rule node corresponding to other (non-zeroth) supplementary predicates. Before constructing a rule for this node, let us determine the arguments for the supplementary predicate. From the rule node, we know that $V_b = (X, XP)$. Searching through the head of rule r_1 we obtain $V_h = (X, Y)$, and through the second subgoal and the rest we get $V_q = (XP, YP, Y)$. Therefore, the supplementary variables V_s are given by

$$V_s = (X, XP) \cap ((X, Y) \cup (XP, YP, Y)) = (X, XP).$$

The rule for this node is

$$\text{sup}1.1(X, XP) \leftarrow \text{sup}1.0(X), \text{par}(X, XP)$$

The predicate sup1.0(X) corresponds to the parent node (node $r_{1,0}$) of the node under consideration, and par(X, XP) is the first subgoal of rule r_1. In general, for a predicate supi. j, the second subgoal in the body of the rule defining supi.j is the jth subgoal of the rule r_j. We next consider the left child of node $r_{1,1}$.

5. Subgoal node sg^{bf}

This is the only IDB goal node in the tree. For this node we generate a rule defining magic predicate m.sg. The arguments of this predicate are the bound arguments (determined by adornment bf) of subgoal sg, i.e. the second subgoal of the rule r_1. This subgoal can be identified by the index stored in the parent node (i.e. node $r_{1,1}$). The body of the rule is the supplementary predicate corresponding to the parent node ($r_{1,1}$), defined earlier. Thus, we have the following rule

$$\text{m.sg}(XP) \leftarrow \text{sup}1.1(X, XP).$$

6. Rule node $r_{1,2}$

Following the right branch of rule node $r_{1,1}$ gives us the last rule node, i.e. node $r_{1,2}$. Like its parent node, we create for this node a rule defining other supplementary predicates. Variables constituting the argument for the predicates are given by

$$V_s = (X, XP, YP) \cap ((X, Y) \cup (P, Y)) = (X, YP).$$

The resulting rule is

$$\text{supl.2}(X, YP) \leftarrow \text{supl.1}(X, XP),\ \text{sg}(XP, YP).$$

Finally, we also generate a rule defining IDB predicate sg that appears in the head of r_1. The rule is

$$\text{sg}(X, Y) \leftarrow \text{supl.2}(X, YP),\ \text{par}(Y, YP).$$

For convenience, we rewrite all magic rules that have been generated as follows:

m.sg(a)
m.sg(X) ← supl.1(X, XP)
sup0.0(X) ← m.sg(X)
supl.0(X) ← m.sg(X)
supl.1(X, XP) ← supl.0(X), par(X, XP)
supl.2(X, YP) ← supl.1(X, XP), sg(XP, YP)
sg(X, X) ← sup0.0(X), person(X)
sg(X, Y) ← supl.2(X, YP), par(Y, YP)

We have thus seen that all magic rules that should be resulted by the magic sets' transformation algorithm of Ullman (1989) can be generated based on a rule/goal graph. An algorithm in the form of pseudocode for generating magic rules by using the rule/goal graph is given in an appendix.

THE CORRECTNESS AND PERFORMANCE OF THE ALGORITHM

We want to show that our algorithm and Ullman's magic sets' algorithm (Ullman 1989) are equivalent in the sense that both algorithms produce the same magic rules as the results of converting the original database rules. To do so, we have to prove that our algorithm produces only the same magic rules as Ullman's algorithm, and that every magic rule produced by the latter is produced by the former. As mentioned above, magic rules resulting from Ullman's algorithm can be classified into five groups as follows:

(i) Rules for magic predicates
(ii) Rules for zeroth supplementary predicates
(iii) Rules for other supplementary predicates

(iv) Rules for IDB predicates
(v) An initialisation rule

We start with an initialisation rule. There is only one initialisation rule, and this rule is created when the root of the rule/goal graph is processed. Each rule of group (i), rules for magic predicates, is created for each IDB predicate appearing in the body of the rule. Our algorithm creates this rule when it process the IDB goal node of the rule/goal graph. Rules of group (ii) contain a predicate of the form supi.0 (i = 0, 1,..., n − 1 where n is the number of database rules) in their heads. In the rule/goal graph, we have rule nodes of the form $r_{1.0}$. By creating a rule for each node r_i.0(i = 0, 1, ...n − 1) we obtain all the rules of group (ii). Similarly, rules of group (iii)contain predicate supi.j(i − 0,1.,,n − 1 and j = 1,2,...,k − 1 where n is as before and k is the number of subgoals in the rule r_i) in the head. These rules can be generated based on rule nodes $r_{i,j}$ of the rule/goal graph. Finally, rules of group (iv), namely modified original rules, can be obtained by creating one rule for each rule node $r_{i,k-1}$, i = 0, 1,..., n − 1 where n and k are as before.

We have thus demonstrated that all the rules of groups (i) to (v) can be created by our algorithm based on the traversal of the rule/goal graph. The next step is to demonstrate that the algorithm creates only the same magic rules as the algorithm of Ullman. Since the involved nodes of the rule/goal graph correspond to particular rules of groups (i) to (v) above, therefore no other rules can be generated. We have thus showed the equivalence of the two algorithms in terms of their functionality. The details of each rule are omitted as they are obvious.

Besides correctness, another important aspect of an algorithm is its performance. As stated above, converting (or rewriting) rules constitutes only one of three phases in the magic sets method. It is clear that the time taken to convert rules is very short compared to the time required to execute the magic rules. Thus, the performance of the algorithm for converting rules is not a major concern. However, to complete a story we will sketch it in the following. It is also useful to mention that the complexity analysis of the entire magic sets algorithm is not a simple task, and could easily become a subject of a separate paper.

Since our algorithm is based on the traversal of a binary tree (converted rule/goal graph), it is easy to show that the time complexity of the algorithm is O(n log n), where n is the number of nodes in the tree. We have seen that the number of nodes depends on the number of subgoals in database rules. Therefore, n is proportional to the number of subgoals.

CONCLUSION

We have shown how to construct a rule/goal graph for a given query and a set of rules. We have also shown the technique to generate magic rules by using the resulting rule/goal graph. The analysis of the correctness and performance of our algorithm for generating magic rules has been presented. An interesting characteristic of the algorithm is that it is simple and clear and yet it manages to derive all and correct rules that are required to answer the query.

Another important characteristic of the algorithm is its time complexity. It has been shown that the time complexity of the algorithm is O(nlogn), which is an acceptable time.

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APPENDIX

Implementation

This section describes the routines for transforming a set of rules into magic rules based on a traversal of a rule/goal graph. During the traversal of the rule/goal graph, we come across two types of nodes, i.e. goal nodes and rule nodes. To manipulate these nodes two routines, namely TraverseSubgoal and ProcessRuleNode, are needed. The former processes goal nodes and the latter processes rule nodes. However, the root node needs a special treatment, although it is one of the goal nodes. The routine that accesses and processes the root constitutes the top-level procedure called TraverseGraph. This procedure is presented as follows:

```
procedure TraverseGraph(root, query);
BEGIN
    /* generate an initialisation rule based on the root */
    print("m.", root ↑predicate);
    /* get bound arguments of the query */
    GetBoundArg(root ↑adorn, query);
    /* access to top-level rule nodes linked to the root */
    entry : = root ↑ptr;
    WHILE entry < > null DO
    BEGIN
        ProcessRuleNode(entry ↑ruleptr, root ↑adorn, null);
        entry : = entry ↑next;
    END
END
```

We assume that a record representing a goal node includes *predicate, adorn,* and *ptr* (pointer) fields. GetBoundArg is a function (routine) to obtain bound arguments of predicate in the query.

ProcessRuleNode

Given a rule node p, an adornment *adorn* for a predicate stored in a goal from which the node p comes out, and a *parent* (rule) node *parent* (exists if the node to be processed has an index i,j, j>0), the procedure *ProcessRuleNode* (p, *adorn, parent*) generates a rule defining a supplementary predicate sup_{ij}, where i.j is an index associated with node p. The following algorithm presented in the form pseudocode defines *ProcessRuleNode* (p, *adorn, parent*).

```
BEGIN
    generate the head of a rule defining $sup_{ij}$;
IF j = 0 THEN
    generate the rule's body for supi.0;
ELSE
    generate the rule's body for supi.j, j>0;
IF p ↑golptr < > null THEN
    TraverseSubgoal(p ↑golptr,p);
IF p ↑rulptr < > null THEN
    ProcessRuleNode(p ↑arulptr,null,p);
ELSE
    generate a rule for an IDB predicate;
END
```

The procedure will be called from two places:

a) inside the procedure TraverseSubgoal, described later, and
b) inside the procedure ProcessRuleNode itself.

The call in (a) generates a rule for the zeroth supplementary predicate, and in this case the adornment *adorn* is required to determine the bound arguments of the rule head. The call in (b) generates a rule for the other supplementary predicate, and for this the above *adorn* is irrelevant.

TraverseSubgoal

This function is relevant only for a goal node repreenting an IDB predicate, for which we generate a rule defining a magic predicate. After generating such a rule, we then access and process all other nodes emanating from this goal node. We present TraverseSubgoal (p,parent), where p and parent represent the goal node and its parent (rule) node respectively, in the form of pseudocode as follows:

```
BEGIN
    IF p contains an IDB predicate THEN
        generate a magic rule;
    /* access to top-level rule nodes */
    entry : = entry ↑ptr;
    WHILE entry < > null DO
        ProcessRuleNode(entry ↑rulptr, p ↑adorn, null);
        entry : = entry ↑next;
    END
END
```

ISSN: 0128-7680

Pertanika J. Sci. & Technol. 2(2): 137-148 (1994)

Penggunaan Garam-Garam Kalium sebagai Agen Pengaktifan Kimia bagi Penyediaan Karbon Teraktif daripada Serepai Batang Kelapa Sawit

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Received 9 July 1993

ABSTRAK

Karbon teraktif daripada serepai batang kelapa sawit telah disediakan dengan kaedah penyulingan merosak dalam keadaan vakum dengan menggunakan beberapa jenis garam kalium, pada pelbagai peratus kandungan, sebagai agen pengaktifan. Perbandingan sifat-sifat kimia dan fizik karbon teraktif yang terhasil menunjukkan bahawa jenis garam kalium dan peratusnya memainkan peranan penting dalam menentukan sifat karbon teraktif yang akan dihasilkan.

ABSTRACT

Activated carbon was prepared from the chips of oil palm trunk by destructive distillation under vacuum, using potassium salts at various concentrations, as the chemical activation agent. The chemical and physical properties of the resulting activated carbon showed that the type and the percentage of potassium salts play an important role which determines the properties of the resulting activated carbon.

Katakunci: Karbon teraktif, batang kelapa sawit, luas permukaan, pengaktifan kimia

PENDAHULUAN

Proses pirolisis kayu atau bahan-bahan lignoselulosa akan menghasilkan empat hasil utama: arang, gas-gas, asid pirolignius dan tar kayu (Klar 1925). Arang yang terhasil boleh dimanfaatkan untuk menghasilkan pelbagai karbon amorfous seperti karbon hitam dan karbon teraktif untuk kegunaan industri dan kehidupan harian, seperti tayar dan barangan getah, pembersihan gula dan air, pemprosesan bahan kimia, bahan farmasi dan lain-lain.

Arang yang terhasil dengan kaedah penyulingan merosak ini boleh diaktifkan untuk penghasilan karbon teraktif. Ini telah dilakukan untuk kayu bakau daripada spesis kurap (*Rhizophora apiculata*) (Jamaluddin 1989) dan minyak (*Rhizophora mucronata*) (Zulkarnain *et al.* 1993).

Pengaktifan karbon boleh dilakukan dengan dua cara, sama ada secara pengaktifan fizikal atau pun pengaktifan kimia. Pengaktifan fizikal biasanya melibatkan penggunaan bahan pengaktif seperti gas karbon dioksida, stim atau pun kombinasi kedua-duanya, sementara pengaktifan kimia melibatkan penggunaan bahan kimia seperti asid fosforik (Jagtoyen *et al.* 1992), garam kalium (Laine and Calafat 1991), zink klorida (Caturla *et al.* 1991) dan sebagainya. Penggabungan kedua-dua kaedah, fizikal dan kimia dengan menggunakan zink klorida sebagai bahan pengaktif telah dilaporkan dapat meninggikan luas permukaan sehingga melebihi 3000 m^2/g (Caturla *et al.* 1991).

Sungguh pun kajian terdahulu menunjukkan bahawa batang kelapa sawit tidak sesuai dijadikan arang disebabkan nilai kalorinya yang rendah (4032 kkal/kg) dan nilai abunya yang tinggi (37.2%) (Lim 1992), kajian mengenai kesesuaiannya sebagai bahan mentah untuk menghasilkan karbon teraktif belum lagi dijalankan. Oleh yang demikian satu kajian telah dijalankan. Disamping itu sifat kimia dan fizik karbon teraktif yang dihasilkan dikaji dari segi pengaruh jenis garam kalium dan peratusnya terhadap luas permukaan karbon teraktif yang dihasilkan.

BAHAN DAN KAEDAH

Karbon teraktif daripada serepai batang kelapa sawit yang dibekalkan oleh PORIM, telah disediakan dengan menggunakan kaedah penyulingan merosak pada keadaan vakum seperti yang telah dipatenkan (British Patent 2086867, 1984).

Sebanyak 6 g serepai batang kelapa sawit bersaiz 0.1 - 1.0 sm yang telah dikeringkan di dalam ketuhar pada suhu 80°C selama seminggu, dimasukkan ke dalam kaca sinter yang kemudiannya dimasukkan ke dalam turus pembakar kuartza. Turus ini kemudiannya dimasukkan ke dalam relau turus.

Turus kuartza kemudiannya divakumkan dan seterusnya dipanaskan sehingga mencapai suhu 500°C. Setelah keadaan ini tercapai, sampel tersebut kemudiannya dipanaskan selama tiga jam. Selepas pemanasan selesai, karbon yang terbentuk dibiarkan menyejuk dan dijadikan serbuk dengan mengayak mengunakan tapis Endecotts 80-100 mesh, dan disimpan untuk pencirian seterusnya.

Impregnasi telah dilakukan dengan menimbang 20 g serepai batang kelapa sawit dan dicampurkan dengan 150 ml larutan garam K_2C_3O dengan peratus kandungan tertentu (Laine and Calafat 1991). Campuran tersebut kemudiannya dipanaskan dalam kukus air sehingga larutan berlebihan terwap keluar. Sampel kemudiannya dikeringkan pada 120°C semalaman di dalam ketuhar. Sampel yang telah terimpregnasi kemudiannya digunakan untuk menyediakan karbon teraktif dengan cara yang sama seperti di atas. Garam-garam kalium lain seperti klorida dan fosfat juga digunakan untuk kajian perbandingan.

Luas permukaan karbon teraktif yang dihasilkan ditentukan dengan menggunakan kaedah iodin (Puri dan Bansal 1965), yang telah dibuktikan dapat memberi nilai luas permukaan yang setanding dengan nilai yang didapati dengan menggunakan kaedah jerapan gas B.E.T. (Rozman 1993). Penentuan logam-logam utama (seperti Na dan Mg) dan surih (Mn, Fe dan Zn) yang terkandung dalam serepai batang kelapa sawit dilakukan dengan menggunakan kaedah pengaktifan neutron, sementara kaedah mikroskop elektron pengimbasan digunakan untuk melihat morfologi serepai batang kelapa sawit dan karbon teraktif yang dihasilkan.

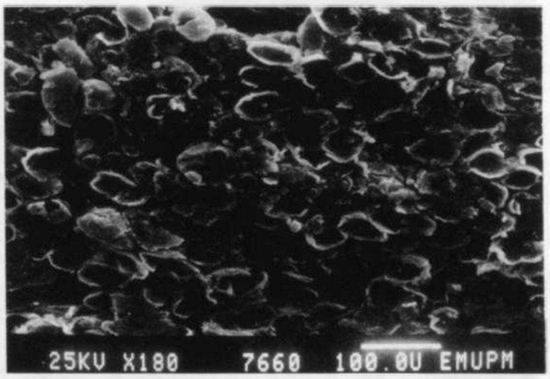
Kandungan lembapan dan pH karbon teraktif yang terhasil ditentukan dengan menggunakan kaedah seperti yang disyorkan oleh SIRIM (SIRIM 1984).

KEPUTUSAN DAN PERBINCANGAN

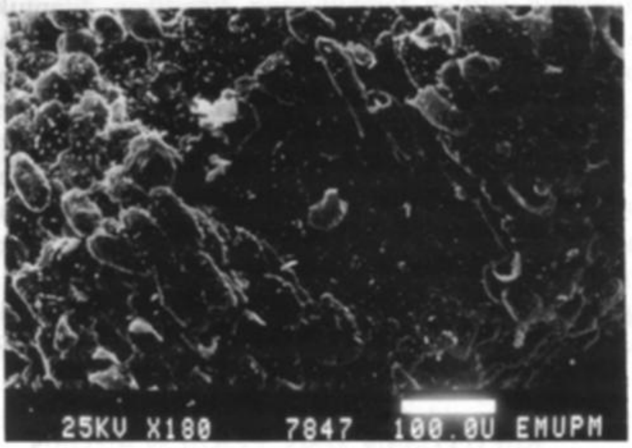
Mikrograf Elektron Pengimbasan

Rajah 1a menunjukkan mikrograf elektron pengimbasan bagi serepai batang kelapa sawit pada pembesaran 180x, sementara *Rajah 1b* menunjukkan serepai batang kelapa sawit yang telah diimpregnasikan dengan 4% larutan kalium karbonat pada pembesaran yang sama. Jika perbandingan *Rajah 1a* dengan *1b* dibuat, jelas menunjukkan bahawa terdapat hablur-hablur garam pada permukaan luar serepai batang kelapa sawit tersebut akibat proses impregnasi yang telah dilakukan. Saiz hablur-hablur garam ini adalah sekitar 2 - 4 µm seperti yang ditunjukkan dalam *Rajah 1c* pada pembesaran 1000x.

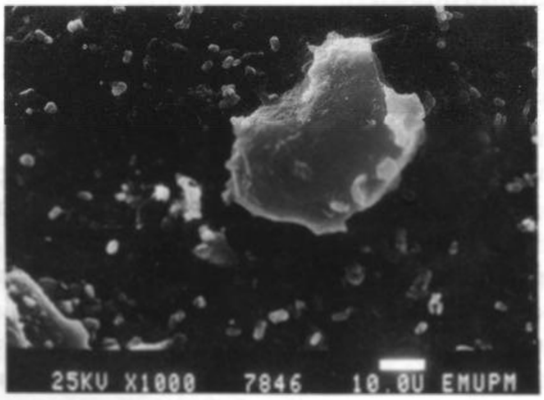
Rajah 1d menunjukkan mikrograf elektron pengimbasan bagi karbon teraktif yang disediakan daripada batang kelapa sawit tanpa pengunaan agen pengaktifan, menunjukkan kehadiran liang-liang asal yang masih kekal walaupun proses pengkarbonan telah dilakukan. Ini menunjukkan bahawa semasa proses pengkarbonan, hanya bahan-bahan meruap sahaja yang dikeluarkan, sementara bahan-bahan lignoselulosa masih kekal seperti sedia kala.



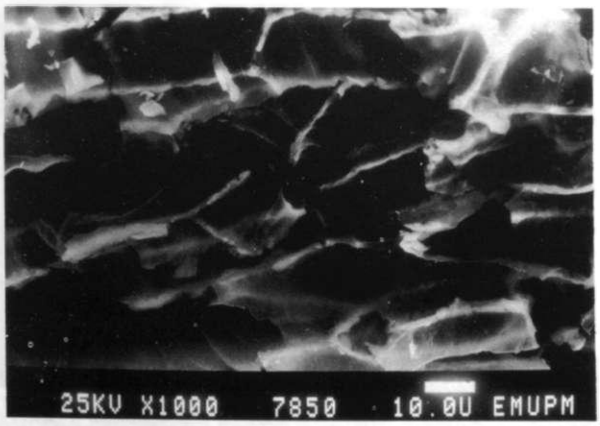
Rajah 1. Mikrograf elektron pengimbasan bagi
(a) Serepai batang kelapa sawit pada pembesaran 180x



(b) Serepai batang kelapa sawit terimpregnasi dengan larutan kalium karbonat pada pembesaran 180x



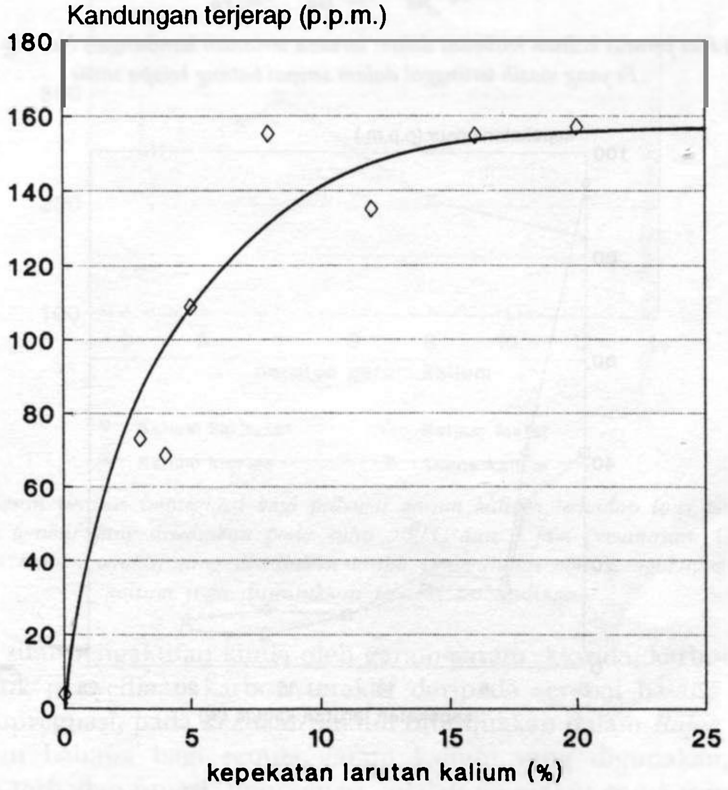
(c) Seperti (b) tetapi pada pembesaran 1000x.
Hablur-hablur kalium karbonat dianggarkan bersaiz di antara 2-4 mm



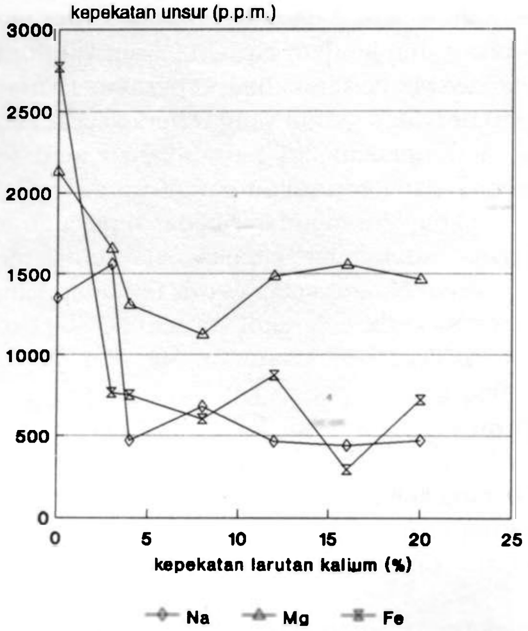
(d) Karbon teraktif yang disediakan daripada serepai batang kelapa sawit

Impregnasi Garam Kalium dan Kesannya terhadap Unsur-unsur Lain

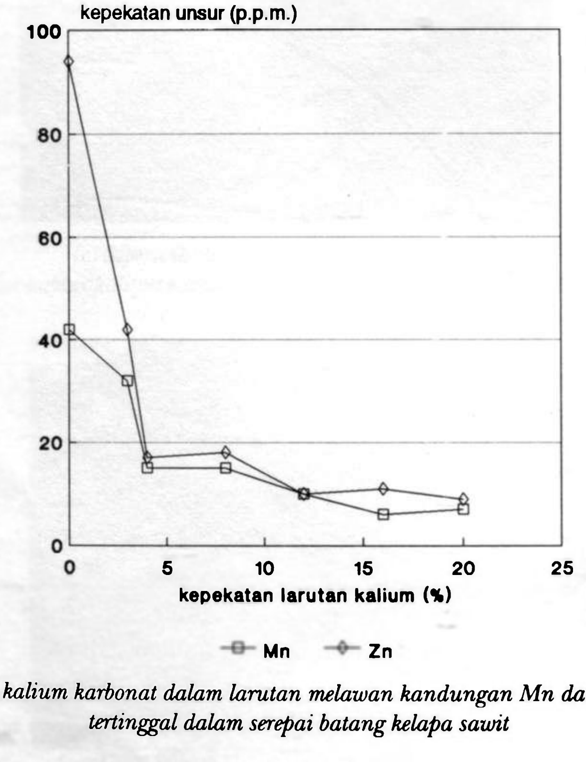
Rajah 2a menunjukkan sifat jerapan larutan garam kalium karbonat ke atas serepai batang kelapa sawit. Pertambahan kepekatan larutan garam tersebut mengakibatkan pertambahan garam yang terjerap secara eksponen. Bentuk isoterma jerapan menunjukkan ciri pertambahan awal secara mendadak bagi bahan penjerap pada kepekatan garam yang rendah dalam larutan dan diikuti dengan bahagian mendatar pada kepekatan garam yang lebih tinggi. Kesan daripada pertambahan kepekatan larutan garam K_2C_3O sebagai agen pengaktifan serepai batang kelapa sawit terhadap kandungan Na, Mg, Mn, Fe dan Zn setelah karbon teraktif terbentuk juga telah dikaji. Pada umumnya didapati bahawa kepekatan Na, Mg, Mn, Fe dan Zn menurun dengan pertambahan larutan garam kalium, seperti yang ditunjukkan di dalam *Rajah 2b* untuk Na, Mg dan Fe, dan *Rajah 2c* untuk Mn dan Zn. Ini menunjukkan bahawa terjadi proses larut lesap unsur-unsur tersebut daripada serepai batang kelapa sawit kepada larutan garam kalium karbonat, dan unsur-unsur yang terlarut lesap ini pada umumnya berkurang dengan pertambahan peratus kalium dalam larutan.



Rajah 2. Impregnasi kalium karbonat dan kesannya terhadap unsur-unsur lain (a) Plot peratus kalium karbonat dalam larutan melawan kandungan kalium yang terjerap pada serapai batang kelapa sawit



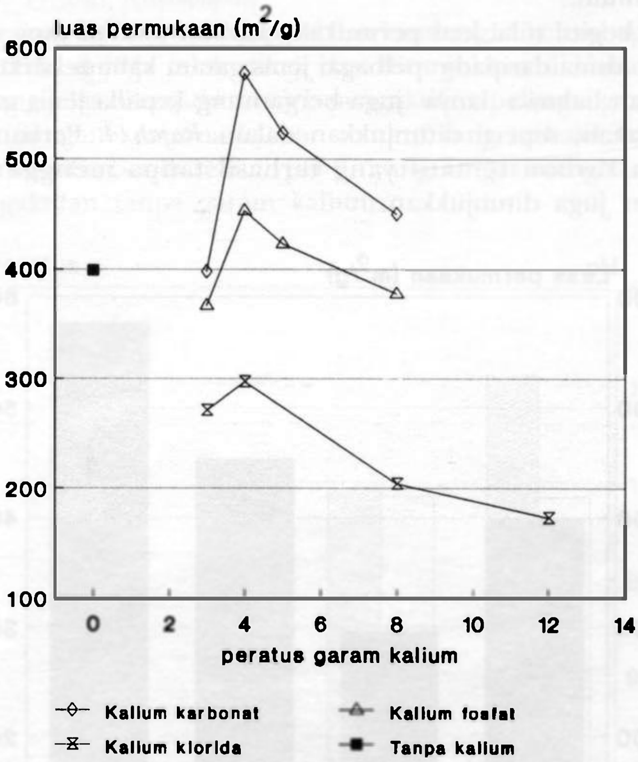
(b) Plot peratus kalium karbonat dalam larutan melawan kandungan Na, Mg dan Fe yang masih tertinggal dalam serepai batang kelapa sawit



(c) Plot peratus kalium karbonat dalam larutan melawan kandungan Mn dan Zn yang masih tertinggal dalam serepai batang kelapa sawit

Kesan Peratus Impregnasi Garam Kalium terhadap Luas Permukaan

Kajian awal menunjukkan bahawa tanpa agen pengaktifan, penyediaan karbon teraktif pada 500°C dengan pemanasan selama 3 jam, menghasilkan karbon teraktif dengan nilai luas permukaan 400 m^2/g. Ini ditandakan di dalam *Rajah 3.* Parameter suhu dan masa pemanasan ini ditetapkan bagi penyediaan karbon teraktif seterusnya. Agen pengaktifan yang terdiri daripada garam-garam kalium pada pelbagai peratus kandungan, dengan proses impregnasinya telah diterangkan, diguna untuk penyediaan karbon teraktif seterusnya.



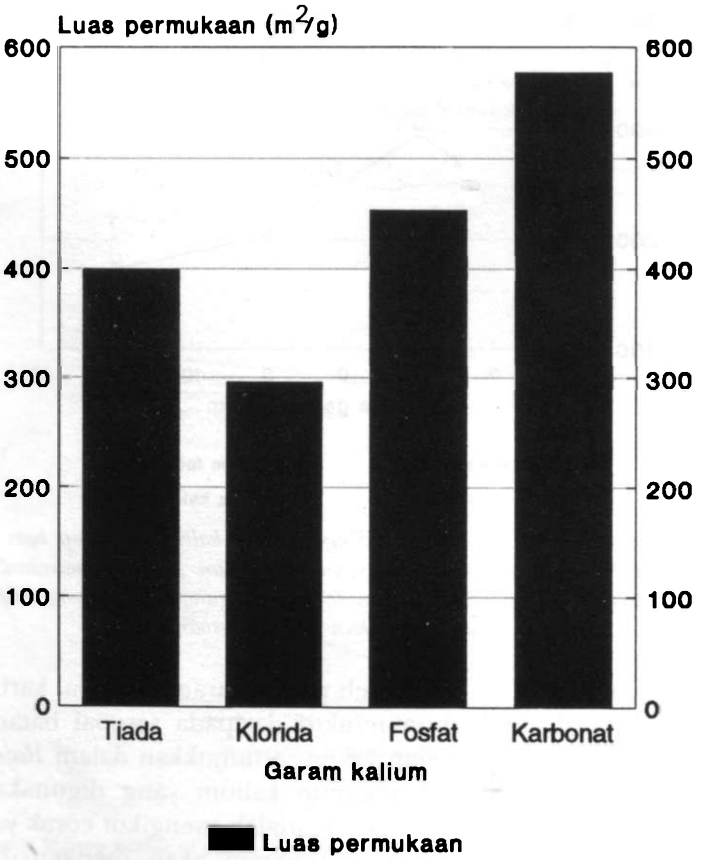
Rajah 3. Kesan peratus impregnasi bagi pelbagai garam kalium terhadap luas permukaan karbon teraktif yang disediakan pada suhu 500°C dan 3 jam pemanasan. Luas permukaan karbon teraktif yang disediakan tanpa penggunaan agen pengaktifan garam kalium juga ditunjukkan sebagai perbandingan

Kesan sifat pengaktifan kimia oleh garam-garam klorida, karbonat dan fosfat untuk penyediaan karbon teraktif daripada serepai batang kelapa sawit terimpregnasi, pada keadaan vakum ditunjukkan dalam *Rajah 3.* Jelas ditunjukkan bahawa bagi semua garam kalium yang digunakan, kesan kepekatan terhadap fungsi impregnasi adalah mengikut corak yang sama, dengan pertambahan peratus muatan garam akan menambahkan luas permukaan karbon teraktif yang dihasilkan. Sebaliknya apabila peratus muatan garam-garam ini melebihi 4%, maka kesan negatif terhadap luas permukaan akan didapati, dengan penambahan muatan garam akan menurunkan nilai luas permukaan karbon teraktif yang akan dihasilkan. Kesan negatif sedemikian adalah berkaitan dengan kesan "hapus terbakar" yang berlebihan bagi bahan-bahan pemula (Laine and Calafat 1991).

Kesan Jenis Garam Kalium terhadap Luas Permukaan Karbon Teraktif yang Terhasil

Rajah 3 juga menunjukkan bahawa untuk semua garam kalium yang digunakan sebagai agen pengaktifan kimia, kandungan 4% adalah merupakan kandungan di mana karbon teraktif yang terhasil mempunyai luas permukaan yang maksimum.

Namun begitu nilai luas permukaan karbon teraktif yang terhasil oleh pengaktifan kimia daripada pelbagai jenis garam kalium berkepekatan 4% menunjukkan bahawa ianya juga bergantung kepada jenis garam kalium yang digunakan, seperti ditunjukkan dalam *Rajah 4*. Perbandingan luas permukaan karbon teraktif yang terhasil tanpa menggunakan agen pengaktifan juga ditunjukkan.

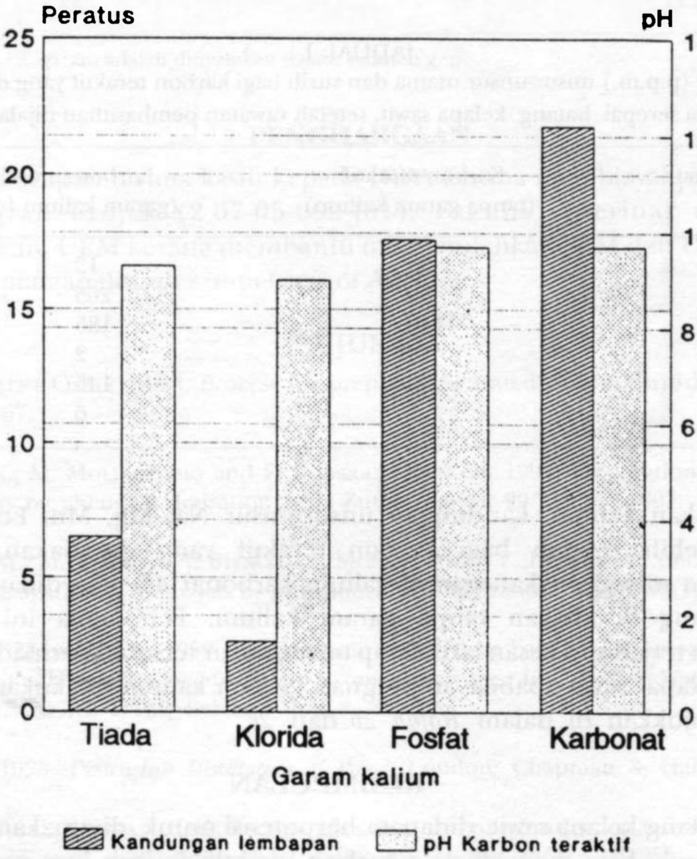


Rajah 4. Kebergantungan luas permukaan optimum karbon teraktif terhadap spesis agen pengaktifan kimia garam-garam kalium

Daripada perbandingan tersebut, garam-garam kalium karbonat dan fosfat menunjukkan kesan positif pengaktifan dengan luas permukaan karbon teraktif yang dihasilkan adalah lebih tinggi jika dibandingkan dengan karbon teraktif yang disediakan tanpa agen pengaktifan. Sebaliknya garam kalium klorida menunjukkan kesan negatif terhadap pengaktifan. Hasil kajian ini sejajar dengan hasil kajian terdahulu, dengan kesan yang serupa juga diperolehi walaupun cara penyediaan karbon teraktif dan sampel yang digunakan berbeza (Laine and Calafat 1991).

Kesan pH dan Peratus Kelembapan

Kesan garam-garam kalium terhadap pH dan kandungan kelembapan karbon teraktif yang terhasil juga telah dikaji dan ditunjukkan di dalam *Rajah 5*. Tiada kesan yang jelas ditunjukkan oleh pengaktifan pelbagai garam kalium terhadap pH, dengan kesemua karbon teraktif yang terhasil memberikan nilai pH yang bersifat bes di sekitar pH 9, yang sangat menghampiri nilai pH bagi pengaktifan tanpa garam kalium.



Rajah 5. Kebergantungan pH dan peratus kelembapan karbon teraktif terhadap spesis agen pengaktifan kimia garam-garam kalium

Sebaliknya bagi pengaktifan oleh garam kalium yang berbeza, karbon teraktif yang terhasil menunjukkan kandungan lembapan yang berbeza. Kandungan lembapan lebih tinggi bagi karbon teraktif yang dihasilkan oleh mangkin garam kalium fosfat dan karbonat, sementara lebih rendah bagi garam klorida jika dibandingkan dengan karbon teraktif yang dihasilkan tanpa agen pengaktifan. Kecenderungan ini sejajar dengan kecenderungan luas permukaan karbon teraktif yang dihasilkan, sebagaimana yang ditunjukkan di dalam *Rajah 4.*

Kandungan Unsur-unsur

Jadual 1 menunjukkan kandungan unsur-unsur utama, Na, K dan Mg serta kandungan unsur-unsur surih, Mn, Fe, dan Zn dalam karbon teraktif yang disediakan daripada serepai batang kelapa sawit sama ada tanpa pengaktifan atau dengan pengaktifan oleh kalium karbonat 4%. Kesemua sampel tersebut telah menjalani rawatan, iaitu dengan merefluks di dalam larutan 0.5M HCl selama tiga hari diikuti dengan air suling dengan penggantian dilakukan setiap hari untuk selama tiga hari berturut-turut.

JADUAL 1

Kandungan (p.p.m.) unsur-unsur utama dan surih bagi karbon teraktif yang disediakan daripada serepai batang kelapa sawit, setelah rawatan pembasuhan dijalankan.

Unsur	Karbon teraktif (tanpa garam kalium)	Karbon teraktif (garam kalium (4%)
Na	55	13
K	80	265
Mg	1340	185
Mn	14	2
Fe	290	145
Zn	7	6

Melainkan kalium, kandungan unsur-unsur Na, Mg, Mn, Fe dan Zn didapati lebih rendah bagi karbon teraktif yang disediakan dengan pengaktifan menggunakan garam kalium karbonat 4% jika dibandingkan dengan yang disediakan tanpa garam kalium. Fenomena ini berlaku disebabkan terjadinya kesan larut lesap unsur-unsur tersebut daripada serepai batang kelapa sawit apabila impregnasi garam kalium dilakukan, seperti yang ditunjukkan di dalam *Rajah 2b* dan *2c.*

KESIMPULAN

Serepai batang kelapa sawit didapati berpotensi untuk digunakan sebagai bahan pemula bagi menyediakan karbon teraktif dengan luas permukaan sederhana, sebagaimana yang ditunjukkan di dalam Jadual 2. Pengaktifan kimia dengan menggunakan kalium karbonat didapati dapat meninggikan luas permukaan sehingga lebih kurang 40% kepada nilai lebih kurang 577 m^2/g, berbanding dengan tanpa pengaktifan oleh kalium karbonat. Didapati juga bahawa kehadiran kalium karbonat sebagai agen pengaktifan telah dapat menurunkan kandungan unsur-unsur surih dan utama bagi karbon teraktif yang dihasilkan.

JADUAL 2

Nilai luas permukaan karbon teraktif yang disediakan daripada serepai batang kelapa sawit dengan menggunakan garam-garam kalium sebagai agen pengaktifan kimia.

	Nilai luas permukaan (m^2/g)		
% garam[a]	K_2CO_3	K_3PO_4	KCl
3	388	**367**	271
4	577	**453**	297
5	523	**423**	-
8	450	**378**	204
12	-	-	173

[a] % garam adalah dinyatakan dalam sebutan g/g.

PENGHARGAAN

Rakaman ucapan terima kasih kepada IRPA kerana membiayai projek ini di bawah gran Projek (2-07-05-009-J01), Fakulti Veterinar dan Sains Perternakan, UPM kerana membantu mengendalikan SEM dan UTN di atas khidmat penganalisisan sampel secara APN.

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ISSN: 0128-7680
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A Parallel AGE Method for Parabolic Problems with Special Geometries

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Received 3 February 1993

ABSTRAK

Kaedah tak tersirat kumpulan berselang-seli (TTKS) merupakan satu kaedah lelaran tak tersirat bagi masalah parabola yang melibatkan domain sekata telah dilaksanakan dalam sistem Sequent S27. Kaedah TTKS ini sesuai bagi komputer selari kerana ia mempunyai tugas-tugas yang terpisah dan merdeka, contohnya blok-blok (2 × 2) yang boleh dilaksanakan serentak tanpa melibatkan satu sama lain. Makalah ini menerangkan pembangunan dan perlaksanaan algoritma selari TTKS. Keputusan-keputusan yang diperolehi daripada perlaksanaan selari ini dibandingkan dengan perlaksanaan secara jujukan.

ABSTRACT

The alternating group explicit (AGE), an explicit iterative method for parabolic problems involving regular domains of cylindrical symmetry is implemented in parallel on a MIMD Sequent S27 system. The AGE method is suitable for parallel computers as it possesses separate and independent tasks, i.e (2 × 2) blocks which can be executed at the same time without interfering with each other. This paper reports the development and implementation of the parallel AGE algorithm. The results from parallel implementation are compared with those of the sequential implementation.

Keywords: parallel AGE, parallel computer, MIMD

INTRODUCTION

Let us consider the following parabolic equation in one-space dimension given by

$$\frac{\partial U}{\partial t} = \frac{\partial^2 U}{\partial r^2} + \frac{\alpha}{r}\frac{\partial U}{\partial r} \qquad (1.1)$$

subject to the initial-boundary conditions

$$U(r, 0) = f(r), \qquad 0 \le r \le 1$$

and

$$\frac{\partial U}{\partial U}(0, t) = 0,\ U(1, t) = 0,\ \text{for } 0 \le t \le T \qquad (1.2)$$

This equation reduces to the simple diffusion equation when $\alpha = 0$ and by putting $\alpha = 1$ and $\alpha = 2$ respectively, it becomes a parabolic problem with cylindrical and spherical symmetry. The application of the AGE algorithm to the heat equation (Evans and Sahimi 1987) is now extended for problem (1.1).

PROBLEM FORMULATION

A uniformly-spaced network whose mesh points are $r_i = i\Delta r$, $t_j = j\Delta t$ for $i = 0, 1, \ldots, m, m+1$ and $j = 0, 1, \ldots, n, n+1$ is used with $\Delta r = 1/(m+1)$, $\Delta t = T/(n+1)$ and mesh ratio $\lambda = \Delta t/(\Delta r)^2$.

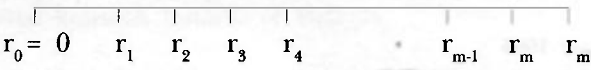


Fig. 1

A weighted approximation to (1.1) at the point (r_i, t_{j+1}) is thus given by Saul'yev (1964),

$$[1 + 2(1+\alpha)\lambda\theta]u_{0,j+1} - 2(1+\alpha)\lambda\theta u_{1,j+1} = [1 - 2(1+\alpha)\lambda(1-\theta)u_{0,j} + 2(1+\alpha)\lambda(1-\theta)u_{1,j} \qquad (2.1)$$

at the axis $r = 0$ and

$$-p_i\theta u_{i-1,j+1} + (1+2\lambda\theta)u_{i,j+1} - q_i\theta u_{i+1,j+1} = p_i(1-\theta)u_{i-1,j} + [1 - 2\lambda(1-\theta)]u_{i,j} + q_i(1-\theta)u_{i+1,j} \qquad (2.2)$$

for $i = 1, 2, \ldots, m$ and points not on the axis, where

$$p_i = (1 - \alpha/2i)\lambda$$

and

$$q_i = (1 + \alpha/2i)\lambda.$$

Following Sahimi and Muda (1988), approximations (2.1) and (2.2) may be written as

$$\begin{bmatrix} a_0 & b_0 & & & & ( ) \\ c_1 & a_1 & b_1 & & & \\ & c_2 & a_2 & b_2 & & \\ & \cdot & \cdot & \cdot & & \\ & & \cdot & \cdot & \cdot & \\ ( ) & & c_{m-1} & a_{m-1} & b_{m-1} & \\ & & & c_{m-1} & a_m & \end{bmatrix} \begin{bmatrix} u_0 \\ u_1 \\ u_2 \\ \cdot \\ \cdot \\ u_{m-1} \\ u_m \end{bmatrix} = \begin{bmatrix} f_0 \\ f_1 \\ f_2 \\ \cdot \\ \cdot \\ f_{m-1} \\ f_m \end{bmatrix}$$

or

$$A\underline{u} = \underline{f} \qquad (2.3)$$

where

$$a_0 = 1 + 2(1+\alpha)\lambda\theta, \qquad a_1 = a = (1 + 2\lambda\theta), \text{ for } i = 1, 2, \ldots, m;$$

$$b_0 = -2(1+\alpha)\lambda\theta, \qquad b_i = -q_i\theta, \text{ for } i = 1, 2, \ldots, m;$$

$$c_i = -p_i\theta, \text{ for } i = 1, 2, \ldots, m;$$

$$f_0 = [1 - 2(1+\alpha)\lambda(1-\theta)]u_{0,j} + 2(1+\alpha)\lambda(1-\theta)]u_{1,j}$$

$$f_i = p_i(1-\theta)u_{i-1,j} + [1 - 2\lambda(1-\theta)]u_{i,j} + q_i(1-\theta)u_{i+1,j}, \quad \text{for } i = 1, 2, \ldots, m-1;$$

$$f_m = p_m(1-\theta)u_{m-1,j} + [1 - 2\lambda(1-\theta)]u_{m,j} + q_m[\theta u_{m+1,j+1} + (1-\theta)]u_{m+1,j}].$$

Note that (2.3) corresponds to the fully implicit, the Crank-Nicolson and the classical explicit methods when $\theta = 1, 1/2$, and 0 respectively with $O((\Delta r)^2 + \Delta t)$, $O((\Delta r)^2 + (\Delta t)^2)$ and $O((\Delta r)^2 + \Delta t)$ accuracy.

Without loss of generality, assume that m is odd. Then, we have an even number $(m+1)$ of internal mesh points at which we seek the solutions of (2.3) along each time level. We now perform the following splitting of A:

$$A = G_1 + G_2 \tag{2.4}$$

where

$$G_1 = \left[\begin{array}{cc:cc:c:cc}
\frac{1}{2}a_0 & b_0 & & & & & \\
c_1 & \frac{1}{2}a & & & & & \bigcirc \\
\hline
 & & \frac{1}{2}a & b_2 & & & \\
 & & c_3 & \frac{1}{2}a & \cdot & & \\
\hline
 & & & & \cdot & \cdot & \\
\hline
 & & & & \cdot & \frac{1}{2}a & b_{m-1} \\
 & \bigcirc & & & & c_m & \frac{1}{2}a
\end{array}\right]_{(m+1)\times(m+1)} \tag{2.5}$$

$$G_2 = \begin{bmatrix} \tfrac{1}{2}a_0 & & & & & & & \\ & \tfrac{1}{2}a & b_1 & & & & () & \\ & c_2 & \tfrac{1}{2}a & & & & & \\ & & & \tfrac{1}{2}a & b_3 & & & \\ & & & c_4 & \tfrac{1}{2}a & \cdot & & \\ & & & & \cdot & \cdot & & \\ & & & & \cdot & \cdot & & \\ & & & & & \cdot & \tfrac{1}{2}a & b_{m-2} & \\ & () & & & & \cdot & c_{m-1} & \tfrac{1}{2}a & \\ & & & & & & & & \tfrac{1}{2}a \end{bmatrix}_{(m+1)\times(m+1)} \qquad (2.6)$$

Following Evans and Sahimi (1987), the following iterative AGE convergent scheme was derived,

$$(G_1 + \hat{r}I)\underset{\sim}{u}^{(k+1/2)} = (\hat{r}I - G_2)\underset{\sim}{u}^{(k)} + \underset{\sim}{f}$$

$$(G_2 + \hat{r}I)\underset{\sim}{u}^{(k+1)} = (G_2 - (1-\omega)\hat{r}I)\underset{\sim}{u}^{(k)}$$

$$+ (2-\omega)\,\hat{r}\underset{\sim}{u}^{(k+1/2)} \qquad (2.7)$$

for any $0 \le \omega \le 2$ and $\hat{r} > 0$ being a fixed acceleration parameter along each intermediate (half-time) level or iterate. A particular choice of $\omega = 0$ gives us the Peaceman-Rachford (PR) scheme and for $\omega = 1$, we obtain the variant due to Douglas and Rachford (DR). Both stable variants are known to have truncation errors of the order $T_{PR} = O((\Delta r)^2 + (\Delta t)^2)$ and $T_{DR}\ ((\Delta r)^2 + \Delta t)$ respectively.

Following Sahimi and Muda (1988) we arrive at the computation of the solution of our geometrical problem:

1) at level (k + 1/2)

$$u_0^{(k+1/2)} = (A_0u_0^{(k)} + B_0u_1^{(k)} + C_0u_2^{(k)} + D_0)/\alpha_0$$

$$u_1^{(k+1/2)} = (A_1u_0^{(k)} + B_1u_1^{(k)} + C_1u_2^{(k)} + D_1)/\alpha_0$$

$$u_i^{(k+1/2)} = (A_iu_{i-1}^{(k)} + Bu_1^{(k)} + C_iu_{i+1}^{(k)} + D_iu_{1+2}^{(k)} + E_i)/\alpha_{i/2}$$

$$\text{for } i = 2, 4, 6, \ldots, m-1 \qquad (2.8a)$$

$$u_{i+1}^{(k+1/2)} = (\bar{A}_iu_{i-1}^{(k)} + B_iu_i^{(k)} + Bu_{i+1}^{(k)} + C_iu_{1+2}^{(k)} + \bar{D}_i)/\alpha_{i/2}$$

$$\text{for } i = 2, 4, 6, \ldots, m-1 \qquad (2.8b)$$

where

$$A_0 = \bar{s}_0 s_0, \quad B_0 = -b_0 s, \quad C_0 = b_0 b_1, \quad D_0 = \bar{s}_0 f_0 - f_1$$

$$A_1 = -c_1 s_0, \quad B_1 = -\bar{s}_0 s, \quad C_1 = -\bar{s}_0 b_1, \quad D_1 = c_1 f_0 - f_1 + \bar{s}_0 f_1$$

$$\bar{A}_i = -c_i c_{i+1}, \quad B_i = -sc_{i+1}, \quad C_i = -sb_{i+1}, \quad \bar{D}_i = \bar{s} f_{i+1} - c_{i+1} f_i$$

$$A_i = -c_i \bar{s}, \quad B_1 = s\bar{s}, \quad C_i = -b_i s, \quad D_i = b_i b_{i+1}, \; E_i = sf_i - ib_i$$

with

$$\bar{s}_0 = \hat{r} + a_0/2, \quad \bar{s} = \hat{r} + a/2, \quad s_0 = \hat{r} - a_0/2, \text{ and } s = \hat{r} - a/2.$$

2) at level (k + 1)

$$u_0^{(k+1)} = (q_0 u_0^{(k)} + d_0 u_0^{(k+1/2)}/\bar{s}_0$$

$$u_i^{(k+1)} = (P_i u_i^{(k)} + Q_i u_{i+1}^{(k)} + Ru_i^{(k+1/2)} + S_i u_{i+1}^{(k+1/2)}/\hat{\alpha}_{(i+1)/2}$$

$$\text{for } i = 1, 3, 5, \ldots, m-2 \tag{2.9a}$$

$$u_{i+1}^{(k+1)} = (\bar{P}_i u_i^{(k)} + P_i u_{i+1}^{(k)} + \bar{Q}_i u_i^{(k+1/2))} + Ru_{i+1}^{(k)}/\hat{\alpha}_{(i+1)/2}$$

$$\text{for } i = 1, 3, 5, \ldots, m-2 \tag{2.9b}$$

where

$$P_i = \bar{s}q - b_i c_{i+1}, \quad Q_i = b_i(\bar{s} - q), \quad R = \bar{s}d, \quad S_i = -b_i d$$

$$P_i = c_{i+1}(\bar{s} - q) \quad Q_i = -c_{i+1} d$$

with

$$q_0 = a_0/2 - (1 - \omega)\hat{r}, \quad q = a/2 - (1 - \omega)\hat{r} \text{ and } d = (2 - \omega)\hat{r}.$$

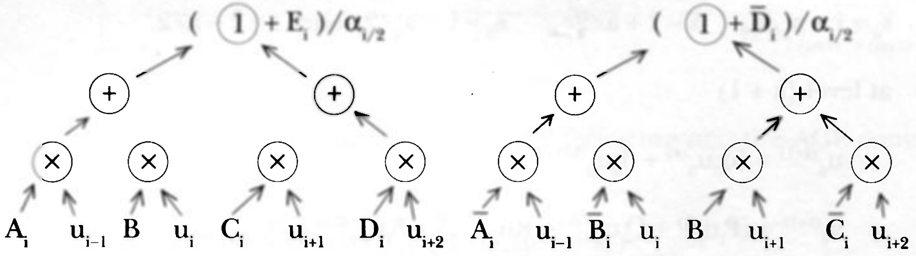
Since the equations 2.8a & 2.8b and 2.9a & 2.9b are explicit, then their solution on a parallel computer is possible.

PARALLEL AGE EXPLOITATION

A parallel algorithm has been developed and implemented to solve the one-space dimension parabolic equation on a MIMD shared memory parallel computer.

The mesh of points (*Fig. 1*) is decomposed into a subset of points, each of which is assigned to a processor. As we have seen, the computation of the solution of our geometrical problem involves iterations of the two sweeps.

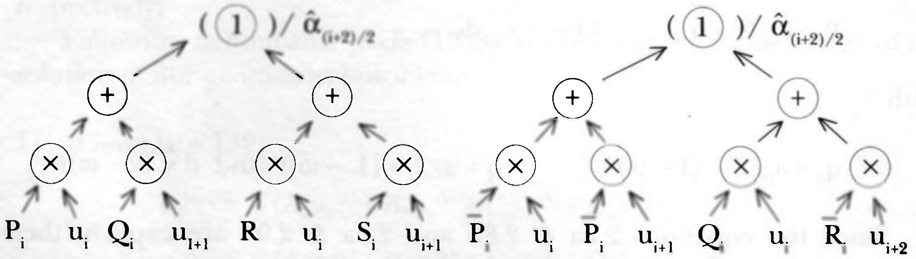
For the first sweep of each mesh point, each computational molecule of equations 2.8a & 2.8b is again assigned to a processor. The computational molecules are then solved depth by depth in parallel in bottom-up order (*Fig. 2(a)*). This method is also known as the balanced binary tree method. The depth of such a tree will be bound by (log n) and the complexity of such an algorithm will be O (log n) where n is the number of nodes. The maximum number of processors employed in this discipline is n/2.



for i = 2, 4, …, m − 1 for i = 3, 5, …, m

Fig. 2(a)

The second sweep is started after the first sweep has been completed. The computational molecules of equation 2.9a & 2.9b are also solved using the same technique (*Fig. 2(b)*). Then a test of convergence is carried out after the second sweep. Further iterations are needed until a prescribed tolerance ε is achieved.



for i = 1, 3, …, m − 2 for i = 2, 4, …, m − 1

Fig. 2(b)

The algorithm for the parallel AGE method is then described as follows.

```
Algorithm begin
for h = 1 to n do
    begin
        T = ht
        k = 0
        while (not converge) and (k < MAX)
            begin
                k=k + 1
                $u_0^{(k+1/2)}$ = ...
                $u_1^{(k+1/2)}$ = ...
                for i = 2 to m−1 in parallel do
                    begin
                        for j = 4 to 7 in parallel do
                            $A_{i,j} = A_{i,2j} * A_{i,2j+1}$
                        for j = 2 to 3 in parallel do
                            $A_{i,j} = A_{i,2j} + A_{i,2j+1}$
                        $u_i^{(k+1/2)} = (A_{i,2} + A_{i,3} + A_{i,4})/\alpha_i$
                    end
            $u_i^{(k+1)}$ = ...
            for i = 1 to m−2 in parallel do
        begin
                        for j = 4 to 7 in parallel do
                            $B_{i,j} = B_{i,2} * B_{i,2j+1}$
                        for j = 2 to 3 in parallel do
                            $B_{i,j} = B_{i,2j} + B_{i,2j+1}$
                    $u_i^{(k+1)} = (B_{i,2} + B_{i,3}) */\alpha_i$
                end
            Test Convergence
            [abs($u_i^{(k+1)} - u_i^{(k)}$) < $\varepsilon$ for all i]
            Replace $u_i^{(k+1)}$ with new $u_i^{(k)}$ for all i
        end
    end
Algorithm end.
```

As the method of divide-and-conquer (Evans and Sutti 1988) is widely applicable in sequential computation, a sequential program is developed and implemented to give its performance in contrast with the parallel.

EXPERIMENTAL RESULTS

Let us consider the cylindrical problem (Mitchell and Pearce 1963)

$$\frac{\partial U}{\partial t} = \frac{\partial^2 U}{\partial r^2} + \frac{1}{r}\frac{\partial U}{\partial r}, \qquad (0 \leq r \leq 1)$$

$$U(r, 0) = J_0(\beta_r),$$

$$\frac{\partial U}{\partial U}(0, t) = U(1, t) = 0, \qquad t > 0$$

where J_0 (βr) is the Bessel function of the first kind of order 0 and β is the first root of $J_0(\beta) = 0$. The exact solution is $U(r, t) = J_0(\beta r)e^{-\beta 2t}$.

This problem is implemented in parallel as well as in sequential on the sequent symmetry S27 system using the strategy discussed above. The programs are written in C language; compiled with the Symmetry C Compiler (version 6.2). The Sequent computer runs on the DYNIX operating system, a version of UNIX 4.2bsd that also supports most utilities, libraries and system calls provided by UNIX System V. Here the Sequent computer supports multi-tasking on 2 processors.

The accuracy of these parallel AGE method results has been verified (*Fig. 3(a)*) with the implicit-sequential results obtained from Sahimi and Muda (1988).

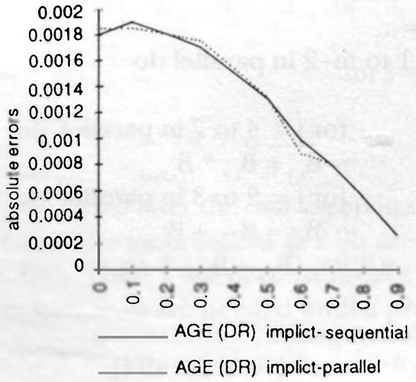


Fig. 3(a). The absolute errors of the numerical solutions to the cylindrical problems (where $\lambda = 1.0$, $t = 1.0$, $\Delta r = 0.1$, $\Delta t = 0.01$, $\hat{r} = 0.9$, $\omega = 1$*)*

In the implementations, the execution time of the two sweeps is obtained with the number of mesh points being increased (Table 1). By comparing the results of the implementations, we notice that the processing times for the parallel strategy are less than those of the sequential strategy (*Fig. 3 (b) & 3(c)*). This is mainly due to the effectiveness of the algorithm which enables a high percentage of the problem to be parallelized (in equations 2.8a, 2.8b, 2.9a and 2.9b).

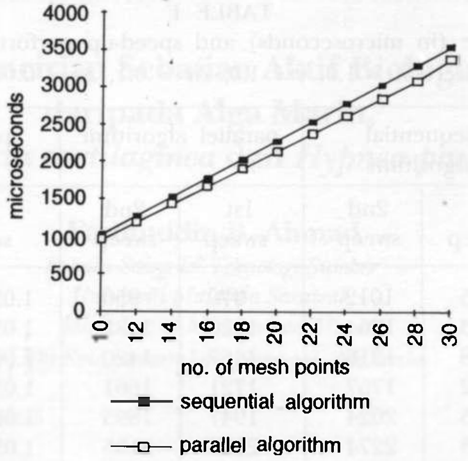


Fig. 3(b). The time execution performance of the first sweep

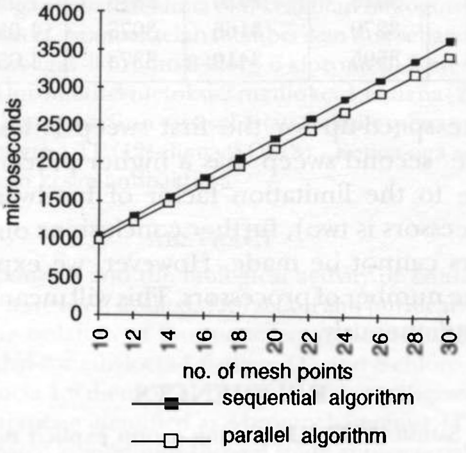


Fig. 3(c). The time execution performance of the second sweep

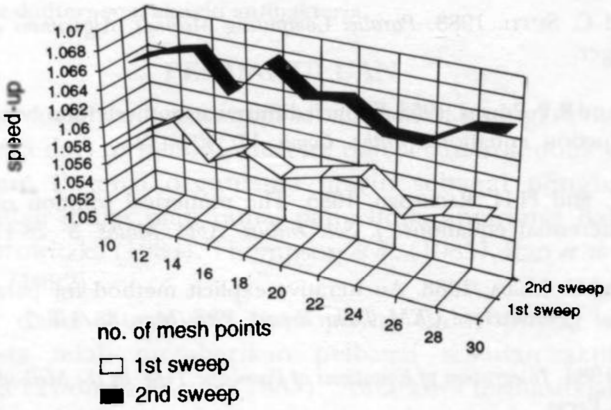


Fig. 3(c). Comparison of the speed-up of the parallel AGE method

TABLE 1
The execution time (in microseconds) and speed-up performance of the parallel AGE method (where $\lambda = 1.0$, $t = 1.0$, $\Delta r = 0.1$, $\Delta t = 0.01$, $\hat{r} = 0.9$, $\omega = 1$)

no. of mesh points	sequential algorithm		parallel algorithm		parallel speed-up	
	1st sweep	2nd sweep	1st sweep	2nd sweep	1st sweep	2nd sweep
10	1035	1012	979	950	1.057201	1.065263
12	1293	1264	1220	1185	1.059836	1.066667
14	1558	1516	1467	1420	1.062031	1.067606
16	1822	1767	1721	1661	1.058687	1.063817
18	2065	2024	1947	1895	1.060606	1.068074
20	2323	2274	2194	2135	1.058797	1.065105
22	2589	2529	2443	2373	1.059763	1.066574
24	2841	2782	2678	2617	1.060866	1.063049
26	3095	3028	2926	2846	1.057758	1.063949
28	3353	3279	3166	3078	1.059065	1.065302
30	3613	3595	3410	3373	1.059531	1.065904

In *Fig. 3(d)*, the speed-up for the first sweep is less than the second. This is because the second sweep has a higher percentage of parallelism than the first. Due to the limitation factor of hardware facilities (that is the number of processors is two), further conclusions on speed-up for more than two processors cannot be made. However, we expect a better speed-up as we increase the number of processors. This will mean more subproblems can be solved simultaneously.

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ISSN: 0128-7680
Pertanika J. Sci. & Technol. 2(2): 159-163 (1994)

Pencirian Sebatian Aktif Biologi daripada Alga Marin, *Laurencia cartilaginea* dan *Hypnea pannosa*

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Received 27 January 1993

ABSTRAK

Alga marin iaitu *Laurencia cartilaginea* dan *Hypnea pannosa* telah dikaji bagi menentukan kandungan sebatian kimia dan keaktifan biologinya. Pengestrakan dan penulenan ke atas *H. pannosa* telah memberikan dua sebatian monoterpena yang dikenalpasti sebagai 3-bromo-8-kloro-6-klorometil-2-metilokta-1,6-diena (**1**) dan 8-kloro-6-klorometil-3-metoksi-2-metilokta-1,6-diena(**2**). Manakala *L. cartilaginea* pula telah memberikan satu sebatian seskuiterpena yang dikenalpasti sebagai 8-bromokamigra-1,11 (12)-diena-9-Ol (**3**). Ketiga-tiga sebatian halogen tersebut menunjukkan kesan antibakteria.

ABSTRACT

The chemical components and the biological activity of *Laurencia cartilaginea* and *Hypnea pannosa* have been studied. Extraction and purification of *H. pannosa* have resulted in the isolation of two monoterpenes identified as 3-bromo-8-chloro-6- chloromethyl-2-methylocta-1,6-diene (**1**) and 8-chloro-6-chloromethyl-3-methoxy-2-methylocta-1,6-diene (**2**). The study of *L. cartilaginea* resulted in the isolation of a sesquiterpene identified as 8-bromochamigra-1,11 (12)-diene-9-Ol (**3**). All the halogenated compounds showed some antibacterial properties.

Katakunci: ***Laurencia cartilaginea*, *Hypnea pannosa*, Rhodophyta, monoterpena, seskuiterpena, aktiviti antibakteria.**

PENDAHULUAN

Kebanyakan alga marin mengandungi sebatian aktif biologi dengan struktur yang berbeza-beza dari terpenoid, steroid, dan sebatian fenolik yang terikat kepada halogen. Potensi organisma marin sebagai penghasil bahan farmaseutikal telah diulas oleh ramai penyelidik, antaranya Baker (1984), Reichelt dan Borowitzka (1984), Thompson *et al.* (1985), Rao *et al.* (1986) dan Ballantine *et al.* (1987).

Rumpai air dalam kumpulan Cyanophyta, Chlorophyta, Phaeophyta dan Rhodophyta telah memberikan pelbagai sebatian aktif terhadap mikroorganisma (Thompson *et al.* 1985). Antaranya termasuklah asid kinik dari *Digenea simplex* sebagai agen antihelmentik, fleksilin dari *Udotea* sp. sebagai antibiotik, sebatian majuskulamida dari *Lyngbya majuscula* sebagai bahan antifungal dan diktyol dari *Dictyota dichomata* sebagai agen antibakteria (Thompson *et al.*, 1985; Ballantine *et al.*, 1987).

Kajian sebatian dari rumpai air laut di Malaysia amat terbatas. Laporan ini akan membincangkan pengekstrakan dan penulenan sebatian dari dua jenis rumpai air iaitu *L. cartilaginea* Yamada (Rhodophyta, Ceramiales, Rhodomelaceae) dan *H. pannosa* (Rhodophyta, Gigartinales, Hypneaceae) yang tertabur secara meluas di perairan pantai sekitar Kudat, Sabah.

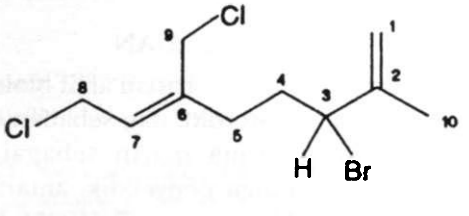
BAHAN DAN KAEDAH

Kaedah Umum

Semua rumpai air laut yang digunakan dalam kajian ini telah dipungut di Pantai Bak-Bak, Kudat secara SCUBA (spesimen rumpai air telah dikenalpasti spesiesnya oleh En. Norhadi Ismail Jabatan Sains Laut, UKM Kampus Sabah). Sampel tersebut setelah dibersihkan, direndam dengan MeOH atau campuran MeOH:CH_2Cl_2 (1:1). *H. pannosa* (150 g) telah diekstrak dengan MeOH. Ekstrak MeOH telah dipisahkan kepada fraksi CH_2Cl_2 dan MeOH. Bahagian yang larut dalam CH_2Cl_2 (2.0 g) telah dilakukan kromatografi turus gel silika dengan pertambahan isipadu dietileter secara berperingkat dalam petroleum ringan. Fraksi-fraksi tersebut telah digabungkan berdasarkan nilai R_f dan telah dipisahkan sekali lagi dengan KLN persediaan menggunakan gel silika dengan sistem pelarut yang sama. Fraksi yang kurang polar telah memberikan sebatian tulen **1** dengan berat 40 mg (2%) dan sebatian **2** dengan berat 52 mg (5%).

Rumpai air *L. cartilaginea* (130 g) pula telah diekstrak dengan 500 ml MeOH CH_2Cl_2 (1 : 1). Bahagian yang larut dalam CH_2Cl_2 (2 g, 1.5%) telah dipisahkan secara turus gel silika menggunakan kecerunan kepekatan dari petroleum ringan ke EtOAc bagi memberikan 12 fraksi. Fraksi 1-3 telah digabungkan dan dilakukan kromatografi turus gel silika dengan sistem pelarut petroleum eter: EtOAc (97 : 3) bagi memberikan sebatian **3.**

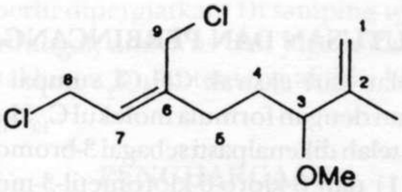
Pencirian Sebatian



1

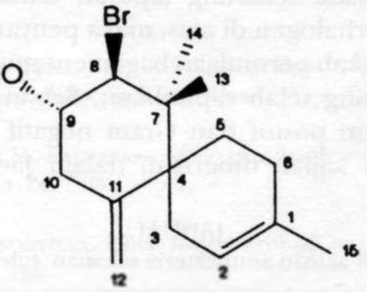
Sebatian 1 : Minyak jernih (Coll dan Wright 1989), $[\alpha]_D$ - 22.5° (c, 0.008); IR, ν maks (filem) 2940, 1640, 1430, 1372, 902, 609 cm^{-1}. ^{1}H-RMN. ($CDCl_3$, 300 MHz) 1.86 (s, 3H, 2-CH_3); 2.12 (m, 2H, H- 4); 2.29 (m, 2H, H-5); 4.06 (s, 2H, H-9); 4.13 (d, 2H, 8.1 Hz, H-8); 4.52 (t, 1H, 7.6 Hz, H-3); 4.90 (s, 1H, H-1); 5.08

(s, 1H, H-1); 5.72 (t, 1H, 8.1 Hz, H-7). ^{13}C-RMN ($CDCl_3$, 75 MHz) : 114.0 (C-1), 142.3 (C-2); 57.9 (C-3); 35.0 (C-4); 31.5 (C-4); 139.2 (C-6); 129.0 (C-7); 39.0 (C-8). 41.2 (C-9); 17.5 (C-10). m/z (%, kelimpahan relatif) 249 (M-Cl, 1.5), 207, 205 (M-Br, 10, 15), 169 (25), 163 (7), 149 (25), 147 (22), 133 (24), 115 (9), 105 (24), 103 (11), 91 (34), 81 (15), 79 (32), 77 (24), 75 (13), 68 (72), 67 (100), 65 (43).



2

Sebatian 2: Minyak jernih (Coll dan Wright 1989), [α]D-16.5° (c, 0.017). IR ν maks (filem), 2980, 1654, 1460, 1275, 1129, 932 cm^{-1}. ^{1}H-RMN ($CDCl_3$, 300 MHz) 1.61 (s, 3H, 2-CH_3); 1.71 (m, 2H, H-4); 2.21 (m, 2H, H-5); 3.16 (s, 3H, 3-OCH_3); 3.45 (dd, 1H, 6.0, 7.5 Hz, H-3); 4.05 (s, 2H, H-9); 4.09 (d, 2H, 8.1 Hz, H-8); 4.87 (s, 1H, H-1); 4.92 (s, 1H, H-1); 5.62 (t, 1H, 8.1 Hz, H-7). ^{13}C-RMN ($CDCl_3$, 75 MHz): 113.5 (C-1), 144.0 (C-2); 85.0 (C-3); 31.1 (C-4); 31.1 (C-5); 141.0 (C-6); 125.5 (C-7); 39.2 (C-8), 40.4 (C-9), 16.3 (C-10); 55.9 (3-OMe). m/z (%) : 236 (M^+, 1), 3); 169 (4); 133 (94); 119 (4); 85 (100); 69 (50); 55 (20); 41 (14).



3

Sebatian 3: Minyak jernih (Wright dan Coll 1990), [α]D-59.0° (c, 0.4), IR ν maks (filem) 3360, 2900, 1445, 1100, 895, 792 cm^{-1}. ^{1}H-RMN ($CDCl_3$), 300 MHz) : 0.96 (s, 3H, 7-CH_3); 1.15 (s, 3H, 7- CH_3); 1.60 (s, 3H, 1-CH_3); 1.85 (m, 2H, H-5); 1.70 dan 1.86 (m, 2H, H-6), 2.05 dan 2.25 (lebar, 2H, H-3); 2.37 (ddt, 11.5, 13.5 dan 1.5 Hz) serta 2.61 (dd, 2H, 5.7 dan 13.5 Hz, H-10); 3.75 (ddd, 1H, 5.7, 10.3 dan 11.5 Hz, H-9); 4.73 (s) dan 5.07 (t, 2H, 1.7 Hz, H-12); 4.46 (d, 1H, 10.3 Hz, H-8); 5.30 (lebar, 1H, 15.2 Hz, H-2). 13C- RMN ($CDCl_3$, 75 MHz): 132.8 (C-1); 119.6 (C-2); 30.5 (C-3); 46.5 (C-4); 25.9 (C-5); 27.6 (C-6); 42.8 (C-7); 77.3 (C-8); 72.0 (C-9); 39.5 (C-10); 143.5 (C-11); 114.9 (C-12); 24.0 (C-13); 18.9 (C-

14); 23.5 (C-15). m/z (%) 298 (4); 283 (10), 219 (32), 157 (13), 147 (26), 145 (48), 135 (45), 133 (35), 121 (38), 119 (100), 117 (18).

Penyaringan Antibakteria

Penyaringan antibakteria telah dijalankan mengikut kaedah yang telah dicadangkan oleh Verpoorte *et al.* (1982). Kepekatan setiap komponen yang telah digunakan adalah 2 mg/ml dalam 30% etanol.

KEPUTUSAN DAN PERBINCANGAN

Fraksi yang kurang polar dari ekstrak CH_2Cl_2 rumpai air *H. pannosa* telah memberikan dua sebatian dengan formula molekul $C_{10}H_{15}Cl_2Br$ dan $C_{11}H_{18}C_{12}O$ yang masing-masingnya telah dikenalpasti sebagai 3-bromo-8-kloro-6-klorometil-2-metilokta 1,6-diena (**1**) dan 8-kloro-6-klorometil-3-metoksi-2-metilokta-1,6-diena (**2**). Ekstrak CH_2Cl_2 *L. cartilaginea* pula telah memberikan satu sebatian tulen dengan formula molekul $C_{15}H_{23}OBr$ yang dikenalpasti sebagai 8-bromo-kamigra-1,11 (12)-diena-9-Ol (**3**). Struktur bagi ketiga-tiga sebatian tersebut telah ditentukan berdasarkan maklumat ^1H-RMN, ^{13}C-RMN, IR dan juga spekstroskopi jisim.

Sebatian **1** dan **2** merupakan sebatian yang pertama kali dilaporkan dari *H. pannosa.* Walau bagaimanapun sebatian-sebatian ini pernah dipisahkan dari rumpai air merah *Chondrococcus hornemannii* (Coll dan Wright 1989). Sebatian **3** pula pernah dipisahkan dari rumpai air *Laurencia majuscula* oleh Wright dan Coll (1990).

Memandangkan tiada sebarang laporan tentang aktiviti biologi bagi ketiga-tiga sebatian berhalogen di atas, maka penyaringan antibakteria telah dilakukan sebagai langkah permulaan bagi menentukan keaktifan biologinya bagi sebatian tulen yang telah dipisahkan. Sebanyak lapan jenis bakteria dalam kumpulan Gram positif dan Gram negatif telah digunakan dalam kajian ini. Keputusan kajian diberikan dalam Jadual 1.

JADUAL 1

Keputusan aktiviti antibakteria sebatian tulen **1**, **2** dan **3**.

Bakteria	Diameter zon perencatan (dalam unit mm)		
	Sebatian 1	Sebatian 2	Sebatian 3
Micrococcus luteus	20.5	21.5	20.0
Streptococcus faecalis	17.0	16.5	18.5
Staphyllococcus aureus	19.0	22.5	21.5
Escherichia coli	8.5	12.0	13.5
Shigella sonnei	12.0	14.5	16.0
Proteus mirabilis	5.0	7.0	9.5
Bacillus subtilis	20.5	19.0	21.5
Klebsiella edwardsii	4.5	6.0	7.5

Jadual 1 di atas menunjukan ketiga-tiga sebatian yang diuji boleh merencat semua bakteria yang digunakan. Bakteria Gram positif memberikan perencatan yang lebih nyata.

KESIMPULAN

Memandangkan ketiga-tiga sebatian yang telah ditulen memberikan aktiviti antibakteria, maka pengekstrakan dan penulenan sebatian-sebatian lain dari rumpai air laut perlu dipergiatkan. Di samping ujian antibakteria, ujian-ujian lain seperti antifungal, antivirus dan juga antitumor perlu dijalankan bagi memperolehi maklumat lanjut tentang aktiviti biologi sebenar sebatian yang telah ditulenkan.

PENGHARGAAN

Pengarang ingin merakamkan terima kasih kepada MPKSN kerana bantuan kewangan melalui Gran R & D No: 4-07-03-011, UKM kerana bantuan kewangan melalui Gran penyelidikan No. 40/87 dan Cik Gomera Jumat yang telah menaip manuskrip ini.

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ISSN: 0128-7680
Pertanika J. Sci. & Technol. 2(2): 165-173 (1994)

Penggunaan Pendekatan Sistem-S dan ESSYNS dalam Analisis Taburan Normal

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ABSTRAK

Makalah ini bertujuan menunjukkan penggunaan kaedah sistem-S dan perisian ESSYNS dalam bidang statistik penghitungan. Pertama, kami akan tunjukkan bagaimana ketumpatan dirumus sebagai sistem-S dan seterusnya bagaimana perwakilan bagi longgokan dan kuantil dapat diterbitkan. Longgokan diperolehi hanya dengan sedikit usaha tambahan dan kuantil dapat dihitung daripada songsangan sistem-S. Perwakilan ini selanjutnya diselesaikan secara berangka dengan menggunakan ESSYNS. Lengkung ketumpatan dan longgokan bagi taburan normal dijana untuk nilai dalam julat (-3,3). Kaedah sistem-S menghasilkan banyak kuantil dalam satu larian komputer. Penggunaan pengitlakan dan penghampiran sistem-S menunjukkan kaedah alternatif ini berguna untuk menganalisis taburan.

ABSTRACT

The purpose of this paper is to illustrate the use of S-systems methodology and ESSYNS software in the area of computational statistics. First, we demonstrate how the densities are formulated as S-systems, then we derive representations for cumulatives and quantiles. Cumulatives are obtained with little extra effort and quantiles are readily calculated from the inverted S-system. These representations are then solved numerically using ESSYNS. The density and the cumulative curves for the normal distribution are generated for the values in the range (-3,3). The S-system method produces many quantiles in a single computer run. The use of S-system generalizations and approximation has shown to be a useful alternative method for analysing distributions.

Katakunci: taburan, sistem-S, persamaan pembeza, perhitungan berstatistik

PENGENALAN

Apabila analisis atau penilaian sesuatu taburan hendak dikaji lazimnya seseorang penyelidik akan terfikir untuk menggunakan pendekatan penakrifan statistik. Sebagai contoh, apabila taburan F hendak dikaji, nisbah dua taburan khi kuasa dua akan digunakan. Pilihan lain yang mungkin adalah perumusan dalam sebutan fungsi-fungsi siri atau fungsi-fungsi khas. Walau bagaimanapun, perwakilan matematik yang padat tidak selalunya sesuai untuk tujuan penghitungan dan adalah lebih berkesan apabila berasaskan perwakilan yang sesuai untuk penilaian berangka walaupun perwakilan tersebut tidak begitu menarik secara matematik.

Sebagai contoh, perhatikan perwakilan yang berlainan bagi fungsi polinomial yang tertentu. Lazimnya, takrifan dalam sebutan kuasa, iaitu $f(t) = \alpha_0 + \alpha_1 t + \alpha_2 t^2 + \alpha_3 t^3$ akan digunakan. Kos penghitungan bagi kuasa adalah tinggi dan kebanyakan buku pengaturcaraan mencadangkan kepada kita untuk menggunakan konsep hasil darab, iaitu $f(t) = \alpha_0 + \alpha_1 \times t + \alpha_2 \times t \times t + \alpha_3 \times t \times t \times t$. Perwakilan ini lebih berkesan berbanding yang pertama tetapi boleh dipertingkatkan secara bererti dengan perwakilan $f(t) = \alpha_0 + (\alpha_1 + (\alpha_2 + \alpha_3 \times t) \times t) \times t$ walau pun ini kurang bermakna secara intuisi. Ini menjelaskan bahawa perwakilan yang berlainan bagi masalah yang sama mempunyai kelebihan masing-masing. Pertama, dapat dilihat dengan baik secara intuisi, keduanya sesuai untuk analisis dengan kertas dan pensil dan yang ketiga mempunyai alkhwarizmi yang optimum.

Melalui makalah ini kita perkenalkan perwakilan matematik yang sesuai untuk analisis secara berangka bagi ketumpatan, longgokan dan kuantil taburan normal. Pertama, akan ditunjukkan bagaimana fungsi ketumpatan dapat dirumus semula kepada satu set persamaan terbitan yang khusus dikenali sebagai sistem-S. Seterusnya ditunjukkan terbitan bagi perwakilan fungsi longgokan dan kuantil. Akhir sekali dipaparkan beberapa hasil penyelesaian berangka yang jitu diperolehi melalui program ESSYNS yang diadakan khusus untuk analisis sistem-S.

PENDEKATAN SISTEM-S

Sistem-S pada peringkat awal digunakan untuk analisis bidang yang lain daripada bidang statistik, iaitu untuk analisis sistem-sistem biologi dan sistem lain yang terurus secara kompleks (lihat Savageau 1976; Savageau and Voit 1982; Voit 1990 untuk rujukan lanjut). Lanjutan daripada itu, sistem-S berjaya digunakan dalam pelbagai bidang termasuk biokimia, imunologi, genetik dan perhutanan (lihat Voit 1991). Sistem-S terdiri daripada set persamaan pembeza peringkat pertama tak linear dengan setiap persamaan mempunyai struktur yang homogen, iaitu terbitan setiap pembolehubah bersamaan dengan beza antara dua hasil darab fungsi hukum kuasa. Jika terdapat n pembolehubah bersandar dan t merupakan pembolehubah bebas, maka sistem-S dapat ditulis seperti berikut:

$$\dot{X}_i = \alpha_i \prod_{j=1}^{n} X_j^{g_{ij}} - \beta_i \prod_{j=1}^{n} X_j^{h_{ij}}$$

$$i \in \{1, 2, \ldots, n\} \qquad (1)$$

dengan $\dot{X}_i = dX_i/dt$; X_i, α_i dan β_i boleh mengambil sebarang nilai nyata tak negatif, dan g_{ij} dan h_{ij} pula boleh mengambil sebarang nilai nyata. Syarat $X_i > 0$ bukan merupakan kekangan yang serius kerana pembolehubah yang negatif boleh dijelmakan kepada positif dengan mudah (Savageau and Voit 1987).

PERUMUSAN SEMULA

Pembolehubah rawak T adalah tertabur secara normal jika dan hanya jika ketumpatan kebarangkalian,

$$n(t; \mu, \sigma) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{t-\mu}{\sigma}\right)^2} \tag{2}$$

$$-\infty < t < \infty, \qquad -\infty < \mu < \infty, \qquad \sigma > 0$$

dan T dirujuk sebagai pembolehubah rawak normal. μ dan σ mewakili min dan sisihan piawai taburan normal. Lanjutan daripada ini, fungsi longgokan normal dapat dinyatakan seperti berikut:

$$F_n(t) = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{t} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2} dx \tag{3}$$

$$-\infty < x < \infty,$$

Terbitan persamaan (2) terhadap t menghasilkan

$$\begin{aligned} \frac{dn(t; \mu, \sigma)}{dt} &= n'(t; \mu, \sigma) \\ &= -\frac{t-\mu}{\sigma^3\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{t-\mu}{\sigma}\right)^2} \\ &= -\frac{t-\mu}{\sigma^2} n(t; \mu, \sigma) \end{aligned} \tag{4}$$

Rumus fungsi ketumpatan kebarangkalian bagi taburan normal ini dapat dibentuk semula sebagai sistem-S dengan menakrifkan dua pembolehubah baru, iaitu $X_1 = t/\sigma^2 + c$ dan $X_2 = n(t; \mu, \sigma)$. Terbitan setiap pembolehubah ini terhadap t akan menghasilkan perwakilan dalam sistem-S dengan $c' = c + \mu/\sigma^2$

$$\begin{aligned} \dot{X}_1 &= \frac{1}{\sigma^2} \\ \dot{X}_2 &= (c' - X_1)X_2 = c'X_2 - X_1X_2 \end{aligned} \tag{5}$$

SONGSANGAN SISTEM-S

Lanjutan daripada hasil keputusan yang langsung, pendekatan sistem-S membenarkan penghitungan ciri-ciri taburan kebarangkalian yang sukar diperolehi dengan cara biasa. Pada bahagian ini akan ditunjukkan bagaimana kuantil dapat dihitung melalui songsangan sistem-S. Apabila taburan normal dibahagikan kepada empat bahagian yang sama maka setiap bahagian ini dikenali sebagai kuantil. Nilai tengahnya dikenali sebagai median dan terdapat dua kuantil di kiri dan kanan median ini. Songsangan sistem-S bermakna menggantikan pembolehubah bebas T dengan pembolehubah yang ditakrif sebagai fungsi longgokan dan setiap pembolehubah sistem-S diungkapkan sebagai fungsi longgokan. Apabila sistem persamaan (7) dibahagikan dengan persamaan terbitan yang terakhir, kuantil bagi taburan normal piawai diperolehi melalui pembolehubah X_1 songsangan. Songsangan sistem-S berhubung dengan kuantil dengan X_3 sebagai pembolehubah bebas dapat dinyatakan seperti berikut:

$$
\begin{aligned}
\frac{dX_1}{dX_3} &= \dot{X}_1 = X_2^{-1} \\
\frac{dX_2}{dX_3} &= \dot{X}_2 = -X_1
\end{aligned}
\qquad (9)
$$

Jika seseorang penyelidik berminat untuk mendapatkan kuantil hujung atas, maka beliau hanya perlu menukar X_3 yang lama kepada $X_3 = 1 - F_z(t)$. Pembolehubah X_1 ditambah dengan pemalar c (katakan c = 1) untuk memastikan pemboleh ubah sistem persamaan sentiasa positif seperti untuk perwakilan taburan normal. Perwakilan sistem-S bagi kuantil hujung atas adalah seperti berikut:

$$
\begin{array}{ll}
\dot{X}_1 = 1 & \\
\dot{X}_2 = X_2 - X_1X_2 & \dot{X}_1 = -X_2^{-1} \\
\dot{X}_3 = -X_2 & \dot{X}_2 = X_1 - 1
\end{array}
\qquad (10)
$$

Apabila pembolehubah bebas X_3 ditingkatkan daripada $F_z(t_0)$ke kuantil K yang diminati, pembolehubah $X_1(K)$ menghasilkan titik-titik penyelesaian termasuk yang ke K dengan bergantung kepada saiz peningkatan, $\pm\Delta t$ yang digunakan. Nilai awal pada $t_0 = 0$ bagi X_{20} ialah $(2\pi)^{-1/2}$ tetapi nilai awal bagi pembolehubah bebas X_1 bersamaan 0.5 dan tidak lagi mengikuti nilai awal t. Misalkan, nilai akhir yang diminati adalah 10^{-6} pada saiz peningkatan yang berlainan (lihat Jadual 1) maka ini dapat diubah dengan menggunakan arahan *Extend.* Jadual 1 menyenaraikan hasil keputusan bagi kuantil taburan normal piawai antara nilai 0.5 hingga 10^{-6}. Kejituan penyelesaian dikawal oleh toleransi ralat setempat maksimum yang boleh dipilih antara nilai 10^{3} hingga 10^{-16}. Toleransi yang digunakan adalah 10^{-12}. Titik penyelesaian yang terjana sehubungan dengan pembolehubah X_1 adalah untuk t + 1. Oleh itu, untuk mendapatkan statistik z berhubung dengan kuantil adalah perlu minus 1 daripada semua titik penyelesaian bagi X_1. Keputusan yang dihasilkan dapat dilihat dalam Jadual 1. ESSYNS tidak memperlihatkan masalah malah memberikan kejituan yang tinggi bagi variat yang mempunyai beberapa sifar di hadapan.

Hasil keputusan yang diperolehi bersamaan dengan sifir statistik (Pearson and Hardley 1976; Murdoch and Barnes 1985) pada kejituan empat titik perpuluhan. Penyelesaian melalui sistem-S bukan sahaja dapat memberi kesemua nilai seperti dalam jadual statistik tetapi juga nilai yang wujud antara mereka pada kejituan yang tinggi. Ini merupakan salah satu kelebihan apabila menggunakan kaedah penyelesaian sistem-S. Sebaliknya jika seseorang penyelidik ingin mendapatkan nilai yang tidak terdapat dalam sifir statistik yang biasa, lazimnya pendekatan interpolasi linear digunakan dan kejituan yang akan diperolehi adalah kurang memuaskan jika kejituan tinggi dikehendaki.

JADUAL 1
Persentil bagi taburan normal (0.5 hingga 0.000001)

α	**kuantil**	α	**kuantil**	α	**kuantil**	α	**kuantil**	α	**kuantil**
0.50	0.00000000	0.050	1.64485363	0.020	2.05374891	0.0010	3.09023231	0.00010	3.71901648
0.45	0.12566135	0.048	1.66456286	0.019	2.07485473	0.0009	3.12138915	0.00009	3.74554859
0.40	0.25334710	0.046	1.68494077	0.018	2.09692743	0.0008	3.15590676	0.00008	3.77501194
0.35	0.38532047	0.044	1.70604340	0.017	2.12007169	0.0007	3.19465105	0.00007	3.80816826
0.30	0.52440051	0.042	1.72793432	0.016	2.14441062	0.0006	3.23888012	0.00006	3.84612614
0.25	0.67448975	0.040	1.75068607	0.015	2.17009038	0.0005	3.29052673	0.00005	3.89059188
0.20	0.84162123	0.038	1.77438191	0.014	2.19728638	0.0004	3.35279478	0.00004	3.94440008
0.15	1.03643339	0.036	1.79911811	0.013	2.22621177	0.0003	3.43161440	0.00003	4.01281081
0.10	1.28155157	0.034	1.82500682	0.012	2.25712924	0.0002	3.54008380	0.00002	4.10747965
0.05	1.64485363	0.032	1.85217986	0.011	2.29036788	0.0001	3.71901648	0.00001	4.26489079
		0.031	1.86629574	0.010	2.32634787			0.000009	4.28835653
		0.030	1.88079361	0.009	2.36561813			0.000008	4.31445101
		0.029	1.89569792	0.008	2.40891555			0.000007	4.34386117
		0.028	1.91103565	0.007	2.45726339			0.000006	4.37758784
		0.027	1.92683657	0.006	2.51214433			0.000005	4.41717340
		0.026	1.94313375	0.005	2.57582930			0.000004	4.46518390
		0.025	1.95996398	0.004	2.65206981			0.000003	4.52638930
		0.024	1.97736843	0.003	2.74778139			0.000002	4.61138233
		0.023	1.99539331	0.002	2.87816174			0.000001	4.75342425
		0.022	2.01409081	0.001	3.09023231				
		0.021	2.03352015						

ISSN: 0128-7680
Pertanika J. Sci. & Technol. 2(2): 175-179 (1994)

Measurement of the Thermal Diffusivity of Materials by Diverging Thermal Wave Technique

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Received 25 August 1993

ABSTRAK

Kami melapurkan penggunaan teknik gelombang terma mencapah untuk mengukur kebauran terma bahan. Inti teknik ini adalah menggunakan maklumat yang terkandung dalam gelombang terma yang dicerap oleh pengesan infra-merah jalur lebar, apabila pengesan ini tersesar daripada punca haba, selepas sahaja pengujaan bahan dengan laser denyut. Kami paparkan beberapa cerapan yang diperolehi dari sampel aluminium, plumbum, kerajang grafit dan grafit zirkonium.

ABSTRACT

The applications of diverging thermal wave technique to measure thermal diffusivities of materials are reported. In essence, the technique makes use of the information content of the thermal waves observed by means of a wide band infrared detector, that laterally displaced from the heat source, following pulsed laser excitation of the materials. Some observations obtained from aluminium, lead, graphite foil, and zirconium graphite samples are presented.

Keywords: thermal wave, thermal diffusivity, diverging, excitation

INTRODUCTION

Thermal wave techniques are increasingly being used to study thermo-physical properties of materials (e.g. Enguehard *et al.* 1990; Imhof *et al.* 1991; Moksin 1993). In this technique, the heat deposited by the laser pulse diffuses to cooler regions of the sample, at rates determined by its thermal diffusivity. Optical properties also play a part in determining the initial temperature gradient within the sample and the way the heated spots emit thermal infrared radiation. Therefore, the thermal waves as detected by the change in the emitted grey body radiation subsequent to pulse laser illumination can be analysed to study the surface and subsurface properties of the materials.

In this paper, the discussion is restricted to thermal waves in which the source of heat and the point of detection are spatially separated, i.e. the thermal waves diverge radially from their source before they can be detected, in contrast to the converging technique described by Enguehard *et al.* (1990).

Fig. 3 and 4 show direct proportionality between r^2 and t_o, as required in theory, except for deviation at short rise-times. The deviations are much more obvious in *Fig. 4*, where slopes of the lines are the least. The superposition of opto-thermal decay and thermal wave signals at short rise-times may be responsible for this. Data for short rise-times in *Fig. 4* were excluded from the least-squares fit calculation.

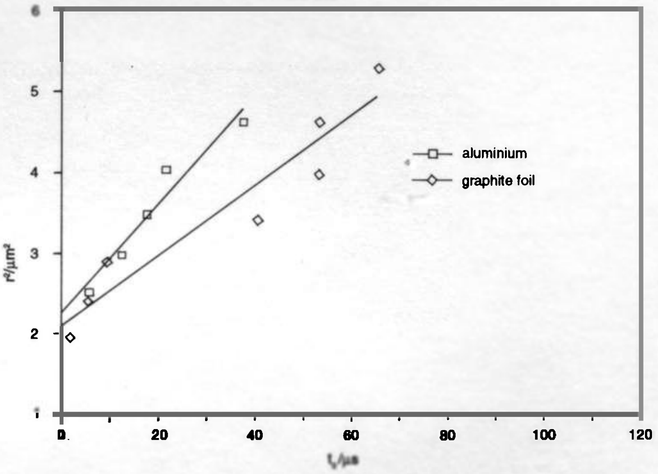

Fig. 3. Square of displacement (r) versus rise-time to for high thermal diffusivity

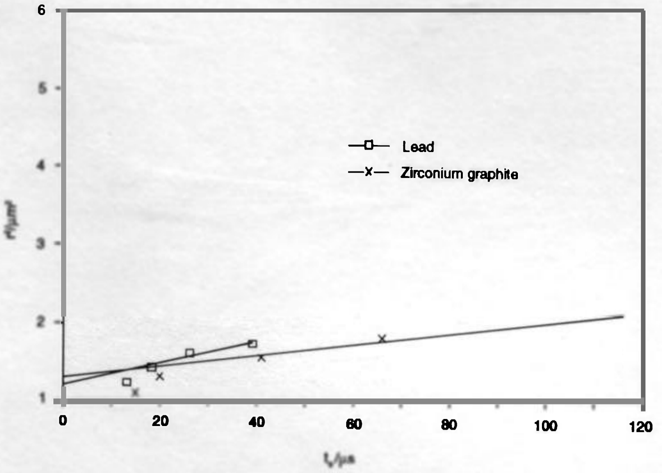

Fig. 4. Square of displacement (r) versus rise-time to for low thermal diffusivity

Table 1 shows that the measured thermal diffusivities are within 16% of the available accepted values. As comparison, the thermal diffusivity measured by Luukkala *et al.* (1982) was found to be 36% lower than the accepted value. The deviation of the measured values are wider as the thermal diffusivities get smaller. Low thermal diffusivities make measurement difficult because insufficient separation between opto-thermal decay and thermal wave can be obtained.

TABLE 1
Measured and accepted values of thermal diffusivities/(10^5 m^2/s)

Sample	Measured	Accepted (from Touloukian *et al.* 1973)
Aluminium	11.21 ± 1.5	9.68
Graphite foil	7.3 ± 0.8	7.89
Lead	2.3 ± 0.6	2.43
Zirconium graphite	1.2 ± 0.2	not available

CONCLUSION

Diverging thermal wave technique was found best for samples of high thermal diffusivities where thermal waves can be observed at appreciable distances from the heating spots. Further work on theoretical description of the thermal waves to account for optical absorption by the samples and reflections at the interface is in progress. However, with the present theoretical and data analysis, thermal diffusivities measured agree reasonably well with the accepted values. With further developments in experiment and theoretical analysis, this could become an important alternative for measuring absolute thermal diffusivities of condensed media.

ACKNOWLEDGEMENTS

We thank the Malaysian government and Universiti Pertanian Malaysia for research support through SLAB and IRPA.

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the plants. Ram and Verloo (1985) reported that the mobility of cadmium increased with progressive acidification of soils. The effect of organic matter on the mobility of cadmium in some Malaysian cocoa-growing soils was earlier investigated by Low and Lee (1991). The mobility, and hence availability, of this metal to plants could also be reduced by the addition of calcium carbonate and phosphate through the formation of insoluble cadmium carbonate and phosphate.

In an attempt to reduce cadmium uptake by cocoa plants, investigations were carried out to study the ability of pH and several inorganic substances to immobilize cadmium in three Malaysian cocoa-growing soils. This paper reports the results of this study.

MATERIALS AND METHODS

The three cocoa-growing soils used were Rengam, Bernam and Malacca. They were collected from Merlimau, Sungai Buloh and Selbourne cocoa estates respectively. Soil samples were taken from ten to fifteen cores in each plot at three different depths of 0-15, 15-30 and 30-45 cm. The soils were air-dried, crushed, passed through a 2 mm sieve and composited.

In the study of the effect of pH on the immobilization of Cd on soils, 20 ml of 20 mg/l Cd solution at a particular pH was added to the soil (0.25 g). Solution pH was adjusted by the addition of HNO_3 or NaOH. After shaking the soil mixture for 24 h, it was centrifuged and the supernatant was analysed for Cd using an ICP-AES (Low and Lee 1991). A control without soil was similarly carried out.

In the immobilization study, 1 g of solution containing 100 µg Cd as $CdCl_2 .H_2O$ was added to the soil (5 g) and the mixture was made up to a total volume of 8 ml with distilled deionised water in a 50 ml test tube. It was then shaken on a gyratory shaker at 100 rpm at room temperature until the mixture turned dry. Each treatment was carried out in duplicate. $Fe(OH)_3$ was prepared by mixing appropriate volumes of standard solutions of $Fe(NO)_3$ and KOH.

The following soil mixtures were investigated:

Treatment

1. Soil + Cd
2. Soil + Cd + $Ca(OH)_2$ (0.2 g)
3. Soil + Cd + $CaCO_3$ (0.2 g)
4. Soil + Cd + K_2CO_3 (0.5 meq)
5. Soil + Cd + $Ca_3(PO_4)_2$ (0.2 g)
6. Soil + Cd + $Fe(NO_3)_3$ (0.5 meq)
7. Soil + Cd + KH_2PO_4 (0.5 meq)
8. Soil + Cd + $Fe(OH)_3$ (0.5 meq)

The effectiveness of the various treatments in immobilizing cadmium was assessed by measuring the amounts extracted from the incubated soils by the following extractants:

(a)	1 N NH_4AcO	(b)	0.5 N $CaCl_2$
(c)	0.5 N NH_4Cl	(d)	0.5 N $Ca(OH)_2$
(e)	0.5 N NH_4AcO	(f)	0.5 N KNO_3

Extraction by 1 N NH_4AcO was carried out by shaking the soil mixture with 20 ml NH_4AcO solution for 1 h (Kiekens *et al.* 1984). The soil mixture was then centrifuged and the supernatant was analysed for its cadmium content using an ICP-AES (Low and Lee 1991). The remaining soil mixtures were shaken individually with the other extractants for 10 minutes after standing for 16 h (Sopsito *et al.* 1982). Cadmium content was analysed as before.

RESULTS AND DISCUSSION

Effect of Extractants

Various extractants have been recommended for the determination of available cadmium in soils (Gerritse and Van Driel 1984; Kiekens *et al.* 1984). Table 1 shows the efficiencies of the various chemicals in extracting cadmium from the three cocoa-growing soils.

TABLE 1

Extractable cadmium content in soils (mg/kg)

Soil	Rengam	Malacca	Bernam
NH_4AcO (1 N)	0.76 (34.0)	0.14 (19.5)	0.26 (7.8)
$CaCl_2$	0.97 (43.5)	0.76 (36.2)	0.62 (18.5)
NH_4Cl	0.25 (11.2)	0.23 (11.0)	0.63 (18.9)
$Ca(NO_3)_2$	0.10 (4.5)	0.39 (18.6)	0.35 (10.5)
NH_4AcO (0.5N)	0.73 (32.7)	0.26 (12.4)	0.36 (10.8)
KNO_3	0.14 (6.3)	0.09 (4.3)	0.28 (8.4)

Values in brackets are % of Cd compared to the total amount present in the soil.

The amount of cadmium extracted depends on the nature of the soil. All the three soils studied were acidic –Rengam (pH = 5.68), Malacca (pH = 5.73) and Bernam (pH = 4.52). The greatest difference in extraction is noted with $CaCl_2$ and KNO_3 . More than 30% of cadmium was extracted using $CaCl_2$ whereas KNO_3 gave less than 15%. This could not be due to the weaker exchange of K^+ compared with Ca^{2+} as $Ca(NO_3)_2$ did not extract very well.

Effect of pH

The amounts of cadmium remaining in the solutions after treatment are given in Table 2. In water the immobilization of cadmium increased with increasing pH in the range of 4.18 – 7.42. The increase in immobilization is not very marked because of the rather restricted pH range. Also, all the tested soils were acidic even though it has been reported that pH is a critical factor in controlling the distribution of cadmium between soil and solute. As the cocoa-growing soils in Peninsula Malaysia are mainly acidic, efforts have to be made to neutralize them in order to reduce mobility and hence availability of cadmium to plants. Similar results were also obtained by Christensen (1984) in the study of cadmium-soil sorption at low concentrations. In the pH interval of 4 – 7.7, the sorption capacity of the soil increased approximately threefold for one unit increase in pH. Zhan (1986) ascribed the immobility of cadmium at higher pH to the co-precipitation of cadmium with $Fe(OH)_3$.

TABLE 2
Effect of pH in Cd sorption in soil (0.25 g soil per 20 ml of 20 mg/l Cd)

Soil/pH	4.18	5.18	6.18	7.42
Rengam	13.66*	12.76	12.40	11.64
Bernam	7.26	6.54	6.18	5.91
Malacca	9.17	9.15	8.03	7.80
Control	19.94	20.19	20.82	20.97

*mg/l

Effect of Immobilization Reagents

The pH of the soils upon the addition of inorganic reagents is shown in Table 3. The most pronounced effect is observed by the addition of $Ca(OH)_2$ and $Fe(NO_3)_3$. $Ca(OH)_2$ rendered all the three soils alkaline, whereas the reverse effect is observed with $Fe(NO_3)_3$. The addition of $Ca(OH)_2$ appears to cause co-precipitation of cadmium on soil particles, and thus reduces cadmium availability to plants. Table 4 shows that almost all the added cadmium was immobilized in the soils regardless of the nature of the extractant with the addition of $Ca(OH)_2$.

TABLE 3
pH of soils upon the treatment of inorganic reagents

No.	Inorganic reagents	Rengam	Bernam	Malacca
Control	H_2O	5.68	4.52	5.73
1.	$CdCl_2$(100 µg)	5.65	4.50	5.72
2.	$CdCl_2 + Ca(OH)_2$(0.2 g)	12.43	12.41	12.26
3.	$CdCl_2 + CaCO_3$ (0.2 g)	7.26	6.63	7.13
4.	$CdCl_2 + K_2CO_3$ (0.5 meq)	8.65	6.79	8.54
5.	$CdCl_2 + Ca_3(PO_4)_2$ (0.2 g)	6.14	5.06	6.34
6.	$CdCl_2 + Fe(NO_3)_3$ (0.5 meq)	2.39	2.53	2.48
7.	$CdCl_2 + KH_2PO_4$ (0.5 meq)	5.01	3.76	5.27
8.	$CdCl_2 + Fe(OH)_3$ (0.5 meq)	4.29	3.70	5.22

TABLE 4
Cadmium immobilization under different treatments
(amount extracted from 100 µg Cd added)

Soil/Treatment	Extractants					
	NH_4ACO(1N)	$CaCl_2$	NH_4Cl	$Ca(NO_3)_2$	NH_4ACO(0.5N)	KNO_3
Rengam control	0.76	0.97	0.25	0.10	0.73	0.14
1	49.71	61.68	71.70	38.10	30.00	10.02
2	3.90	0.82	2.48	0.67	1.32	0.22
3	16.76	12.58	8.18	1.73	6.43	0.48
4	14.08	4.98	3.43	1.37	6.43	0.48
5	12.36	20.83	10.98	6.02	4.75	0.72
6	83.00	78.58	102.25	75.00	63.80	102.50
7	31.64	59.33	46.75	24.75	15.28	3.68
Malacca control	0.41	0.76	0.23	0.39	0.09	0.26
1	53.82	51.13	59.18	35.75	30.40	13.60
2	5.64	0.88	2.43	0.32	1.34	0.38
3	25.44	14.26	10.75	2.55	8.85	0.78
4	17.66	3.43	3.84	0.75	3.75	1.71
5	17.94	17.55	12.38	6.00	4.20	1.59
6	87.06	60.53	82.25	67.20	63.48	92.70
Bernam control	0.26	0.62	0.63	0.35	0.28	0.36
1	62.78	61.90	102.0	52.55	47.24	69.61
2	2.02	0.26	1.38	0.66	0.58	0.27
3	12.32	85.90	7.81	1.11	19.01	0.72
4	38.28	50.12	51.06	23.70	18.00	6.22
5	13.64	25.12	27.74	13.33	9.44	4.41
6	82.70	79.93	101.32	67.82	73.76	102.90
7	52.50	71.42	100.27	54.40	39.44	75.67
8	71.61	77.80	105.47	65.73	55.86	88.54

The addition of $Fe(NO_3)_3$ caused the pH of the soils to drop below 3. This could cause the cadmium to be in a mobile state. Some inorganic materials gave 100% recovery of added cadmium, indicating non-sorption of cadmium in soils. In general, $CaCO_3$ is more efficient than K_2CO_3 in immobilizing cadmium in Rengam and Malacca soils. $Ca_3(PO_4)_2$ is more efficient in immobilizing cadmium than KH_2PO_4 in all the tested soils. $Fe(NO_3)_3$ is not useful as an immobilizing agent. In some cases this chemical has a negative effect by releasing the cadmium in the soil, probably caused by its low pH and competition between Cd^{2+} and Fe^{3+} for immobilization reaction sites. The reaction between Cd^{2+} and CO^{2-}_3 and PO^{3-}_4 and other anions in the soil-water system is much more complex than in simple solution. It is due to the various possible reactions of cations and the anions and the soil particles. Precipitation of cadmium as $CdCO_3$ and $Cd_3(PO_4)_2$ is generally not considered significant, as in most cases solubility product could not have been attained. Nucleating effect of soil particles facilitates the surface precipitation of cadmium with the carbonates and the phosphates. A two-stage mechanism is thought to be involved in the sorption. The initial step involves the replacement of the counter cation (Ca^{2+} and Mg^{2+}) by Cd^{2+}. This is followed by chemisorption of Cd^{2+} on CO^{2-}_3 and PO^{3-}_4. The sorption of cadmium by $Fe(OH)_3$ involves the replacement of Cd^{2+} with the surface hydroxyl ions with the release of H^+, followed by chemisorption to form Cd–O bonds (Mckenzie 1980).

CONCLUSION

It is concluded that pH plays an important role in the immobilization of cadmium in soils. Addition of $Ca(OH)_2$ is useful both in neutralizing the acidity of the soil and also in reducing the immobility and hence availability of cadmium to plants. Carbonates and phosphates can also influence cadmium mobility in soils, though to a lesser extent than $Ca(OH)_2$.

ACKNOWLEDGEMENT

The authors are grateful to Majlis Penyelidikan Kemajuan Sains Negara, Malaysia, for their financial support (grant no. 04-07-05-017).

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ISSN: 0128-7680
Pertanika J. Sci. & Technol. **2**(2): 189-196 (1994)

The Use of NMR in Quantitative Determination of Oil and Water in Emulsions

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Received 8 May 1992

ABSTRAK

Teknik resonans magnet nukleus digunakan untuk menentukan kuantiti air dan minyak di dalam beberapa emulsi minyak/air. Kaedah ini menggunakan urutan denyut perolihan songsangan untuk menghasil dan mengukur amplitud gema-gema spin pada sela masa tak linear. Suhu dan frekuensi yang digunakan ialah pada 24.5°C dan 2.5MHz. Kuantiti tiap-tiap komponen diperolehi daripada pemadanan data kepada model tak linear yang mengandungi satu atau pun dua eksponen. Bagi n-hexadecane/air dan minyak paraffin/air relaksasi bersesuaian dengan model dua keadaan tak bertukaran. Amaun setiap bahagian boleh ditentukan dengan baik daripada amplitud-amplitud signal. Walau bagaimanapun, minyak zaitun menunjukkan relaksasi berlainan dan lebih komplek. Perbezaan nisbah amplitud signal dengan yang diperolehi dari kaedah timbangan dibincang.

ABSTRACT

Nuclear magnetic resonance techniques have been used to determine quantitatively the amount of water and oil in several oil/water emulsions. The technique utilizes the inversion recovery pulse (IR) sequence to produce and measure the amplitude of the spin echoes at non-linearly spaced time intervals. In this study, the temperature and the operating frequency were 24.5°C and 2.5MHz respectively. The quantity of each component was determined by fitting the data to non-linear models consisting of either one or two exponentials. For n-hexadecane/water and paraffin oil/water, the relaxation behaviour conforms to the two-state non-exchange model. The amount of each constituent could be estimated fairly accurately from the signal amplitudes. Olive oil emulsion, however, appears to be more complex. The difference between signal amplitude ratio and that obtained by weighing is discussed.

Keywords: emulsion, relaxation, nuclear magnetic resonance.

INTRODUCTION

The last twenty years have witnessed a tremendous development in pulsed nuclear magnetic resonance (NMR) techniques in various fields of research and applications. The relaxation times and the proton density have been measured and applied under various conditions to elucidate the state of water in tissues and industrial products (Mathur-De Vre 1984). Fat and water content as well as their distribution in biological samples have been determined by NMR methods (Smith 1986).

Conventionally, fat or oil content is determined by solvent extraction, and water content by drying method. Both processes are obviously tedious and time-consuming. In this paper, a pulsed NMR technique to estimate the quantity of oil and water in emulsions is described. Previously, oil and water components in an emulsion were determined from the spin-spin relaxation signal (Jones 1988). In the present report, the quantity of each component was obtained through computer analysis of the data taken from the spin-lattice relaxation measurements.

MATERIALS AND METHODS

Sample Preparation

Emulsions of various composition were prepared from paraffin oil/water, n-hexadecane/water and olive oil/water. A small amount of Cu^{2+} ions (about 1×10^{20} per cc) was added to the water phase to reduce the relaxation times of pure water from about 3 seconds (Krynick 1966) to about 200 millisecond. A mixture of emulsifying agents - Tween 20 (polyoxyethylene sorbitan monolaurate) and Span 80 (sorbitan monooleate) - was used to stabilise the emulsions. Independent experiments indicated that at a concentration of 5% (v/v), the mixture had no profound effect on the relaxation times T_1 and T_2

Experimental

All measurements were carried out on a home-built pulsed NMR spectrometer at the Department of Bio-Medical Physics and Bio-Engineering, University of Aberdeen. The resonance frequency and temperature were 2.5MHz and 24.5°C respectively. The signal intensity consisting of echo amplitude was obtained by using the modified inversion recovery pulse sequence [180°–τ–90°–180°–Echo–]. The delay time τ was varied non-linearly from 2 ms to 200 ms, with 31 data points. Since the signal originates from two kinds of non-exchangeable spins, the most appropriate expression for the signal decay is

$$S(\tau) = A + Q_1 e^{-\tau/T} 11 + Q_2 e^{-\tau/T^{12}}$$

This equation is a solution of the phenomenological Bloch equations (Bloch 1946) with suitable initial conditions (Salleh 1991); Q_1 and Q_2 correspond to the quantities of each spin, while T_{11} and T_{12} are their respective relaxation time constants. The constant A is added to take into account the errors arising from field offset, base line shift and from electronic noise (Sass and Ziesson 1977; Weiss and Ferreti 1985).

Data Analysis

The method of least-squares, using the Gauss-Newton algorithm (Gill 1978) was used to fit the data to the above equation. The fitting procedure simultaneously yielded Q_1, Q_2, T_{11} and T_{12} including the estimation of the error. The fractional amplitude

$$k = \frac{Q_1}{Q_1 + Q_2} \quad \text{or } k = \frac{Q_2}{Q_1 + Q_2}$$

was calculated and compared with the fractional amount

$$F = \frac{W_1}{W_1 + W_2} \quad \text{or } F = \frac{W_2}{W_1 + W_2},$$

where W_1 and W_2 were the weights of each component obtained by physical method.

RESULTS

Fig. 1 shows the relaxation intensity decay curve for the n-hexadecane/water emulsion at 50%. The solid line is the fitted curve, while the cross signs are the experimental data points. *Fig. 2* illustrates the same data but fitted to the single component decay. It is obvious that fitting the data to the two-component equation is better than fitting it to a single decay equation.

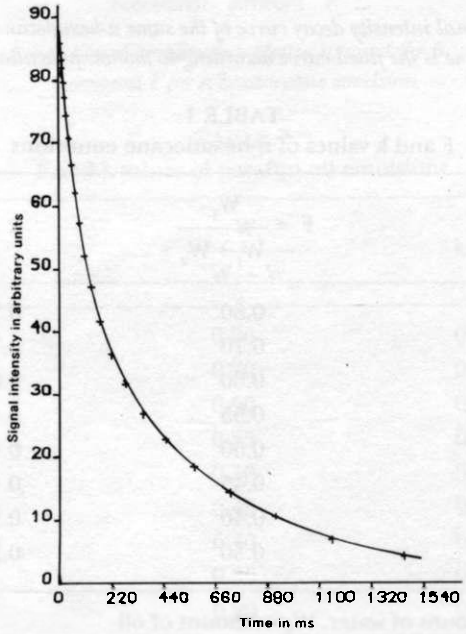

Fig. 1. Signal intensity decay curve of n-hexadecane emulsion. The solid line is the fitted curve according to the equation in the text

Table 1 shows the fractional amount of water obtained experimentally compared with that from weighing.

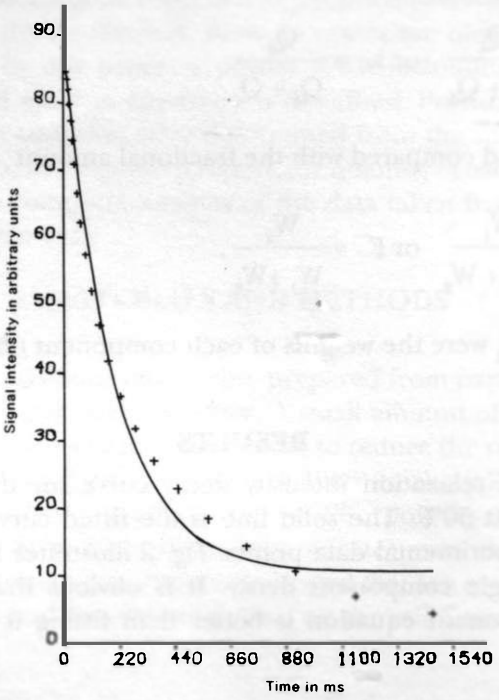

Fig. 2. Signal intensity decay curve of the same n-hexadecane emulsion. The solid line is the fitted curve according to monoexponential expression

TABLE 1
F and k values of n-hexadecane emulsions

Emulsion	$F = \frac{W_1}{W_1 + W_2}$	$k = \frac{Q_1}{Q_1 + Q_2}$
E75	0.80	0.78 ± 0.06
E76	0.70	0.70 ± 0.05
E77	0.60	0.60 ± 0.03
E81	0.55	0.46 ± 0.02
E68	0.50	0.47 ± 0.02
E8	0.45	0.47 ± 0.03
E78	0.40	0.39 ± 0.01
E79	0.30	0.27 ± 0.02

W_1 = amount of water, W_2 = amount of oil

Fig. 3 illustrates the k values plotted against F. The slope and the coefficient of regression were found to be 1.01 and 0.99 respectively. The intercept is almost zero. Thus, a k value can be used as an estimate of F with an error of 2%. Table 2 shows the results obtained from paraffin oil emulsions. A linear relationship is again observed between k and F (*Fig. 4*). The slope and the coefficient of regression were 0.96 and 0.99 respectively.

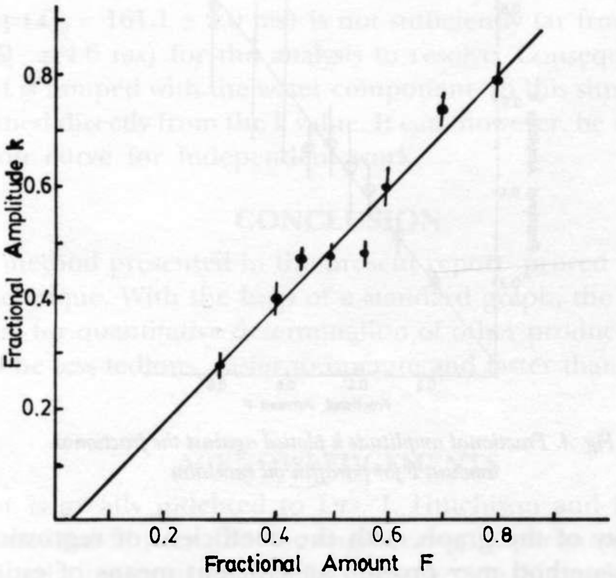

Fig. 3. Fractional amplitude k plotted against the fractional amount F for n-hexadecane emulsion

TABLE 2
F and k values of paraffin oil emulsions

Emulsion	$F = \frac{W_1}{W_1 + W_2}$	$k = \frac{Q_1}{Q_1 + Q_2}$
E90	0.80	0.82 ± 0.19
E91	0.70	0.68 ± 0.19
E92	**0.60**	0.69 ± 0.22
E93	**0.55**	0.48 ± 0.06
E94	**0.50**	0.49 ± 0.09
E95	**0.45**	0.43 ± 0.10
E96	0.40	0.37 ± 0.06
E97	0.30	0.29 ± 0.05
E98	0.20	0.18 ± 0.02

From the above observations it was concluded that the spin-lattice relaxation of n-hexadecane and paraffin oil emulsions obeys the model expressed by the equation. In this situation, protons of the oil and those of the water relax independently, giving rise to two signals which can be separated through the decomposition procedure. Such a phenomenon is an indication of a two-state-non-exchange model.

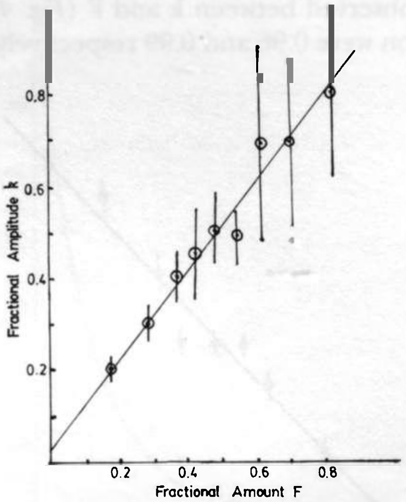

Fig. 4. Fractional amplitude k plotted against the fractional amount F for paraffin oil emulsion

The linearity of the graph, with the coefficient of regression of $\simeq$ 1, shows that the method may provide an efficient means of estimating the amount of each constituent in the emulsions with reasonable accuracy.

Table 3 shows the results of the analysis of olive oil emulsions. The T_1 of olive oil and water are 116.6 ± 3.1 ms and 256.9 ± 4.6 ms respectively.

TABLE 3
F and k values of olive oil emulsions

Emulsion	$F = \frac{W_1}{W_1 + W_2}$	$k = \frac{Q_1}{Q_1 + Q_2}$
E210	0.20	0.21 ± 0.10
E211	0.30	0.32 ± 0.13
E212	0.40	0.32 ± 0.09
E213	0.45	0.38 ± 0.11
E214	0.50	0.40 ± 0.01
E215	0.55	0.48 ± 0.09
E216	0.60	0.49 ± 0.05
E217	0.70	0.52 ± 0.08
E218	0.80	0.58 ± 0.17

Pure oil T_{11} = 45.8 ± 3.0 (ms); T_{12} = 161.1 ± 9.0 (ms); k = 0.56 ± 0.12

It was observed that the variation of k with F for olive oil emulsions is also linear (not shown) with the coefficient of regression of 0.97. However, it does not follow a 1:1 correspondence. The slope is 0.62. The unexpectedly low k values, especially at high oil composition, may be due to the existence of two classes of spins in the oil itself, slow and fast. This is indicated in the last row of the table where, in pure form, the oil reveals two components with equal amplitudes (k = 0.56 ± 0.12). The time constant of the slow component (T_{12} = 161.1 ± 9.0 ms) is not sufficiently far from that of water (T_1 = 256.9 ± 4.6 ms) for the analysis to resolve. Consequently, the slow component is lumped with the water component. In this situation, F cannot be determined directly from the k value. It can, however, be used to prepare a calibration curve for independent work.

CONCLUSION

The NMR method presented in the present report proved to be a reliable and fast technique. With the help of a standard graph, the technique may be extended for quantitative determination of other products. The method is found to be less tedious, easier to operate and faster than the traditional procedure.

ACKNOWLEDGEMENTS

The author is greatly indebted to Drs. J. Hutchison and M.A Hutchison of the Biomedical Physics and Bio-engineering Department, University of Aberdeen for their interest and fruitful discussions in this work. The assistance of Puan Mariah Hj. Ahmad, Department of Physics, Universiti Pertanian Malaysia in typing the manuscript is greatly appreciated.

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ISSN: 0128-7680
Pertanika J. Sci. & Technol. 2(2): 197-206 (1994)

Removal of Zinc by the Moss *Calymperes delessertii* Besch

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Received 23 September 1993

ABSTRAK

Kebolehan satu lumut, *Calymperes delessertii* Besch, untuk menyinkir zink daripada larutan telah dikaji. Dalam eksperimen kelompok, parameter-parameter yang telah dikaji termasuk kesan pH dan kepekatan awal larutan zink pada pengerapan. Satu siri eksperimen turus telah dilakukan untuk mengkaji system ini di bawah keadaan dinamik. Model 'bed depth service time' (BDST) yang dicadangkan oleh Hutchins telah digunakan dengan kejayaan kepada sistem ini. Eksperimen 'fixed bed' pun dijalankan dengan menggunakan air-buangan dari satu kilang penyaduran zink. Keputusan menunjukkan turus lumut boleh digunakan sebagai satu sistem pembersih untuk menyinkir zink daripada air-buangan pengelektrosaduran.

ABSTRACT

Studies were conducted to assess the capability of a moss, *Calymperes delessertii* Besch, to remove zinc from solutions. In the batch experiments, parameters studied included effect of pH and initial zinc concentration on sorption. A series of fixed bed experiments were performed to study the system under dynamic conditions. The bed depth service time (BDST) model proposed by Hutchins was successfully applied to the system. The fixed bed experiments were also carried out using wastewater from a zinc plating factory and results indicated that moss columns could be used in a clean-up system to remove zinc from electroplating wastewater.

Keywords: moss, zinc, sorption, uptake, simulated wastewater, electroplating wastewater, BDST model.

INTRODUCTION

Heavy metals represent a major risk to the environment because of their toxicity. Their removal from water supply and wastewater is thus of utmost importance.

Zinc, one of the heavy metals, is used in the production of non-corrosive alloy, brass, in galvanizing steel and iron products and in electroplating industries. The problems associated with ingestion of zinc are well documented (Elinder 1986).

Various methods have been proposed for the removal of zinc from the wastewater of the metal finishing industries. They include the use of evaporation, reverse osmosis and precipitation as hydroxides. These methods are, however, either costly and complicated or incomplete in metal removal. Hence the search for more efficient and economical means of zinc removal continues.

The use of bryophytes as a sorbent of metal ions in wastewater has not been fully investigated. Mosses appear to be suitable sorbents for heavy metals because they possess several interesting properties (Johnson 1980). The cell wall has a high polyuronic acid content which makes moss a very good natural ion exchanger. In addition, the highly reduced presence or absence of cuticle in the moss means the ions have direct access to the cell wall.

Ruhling and Tyler (1970) reported that woodland moss, *Hylocomium splendens*, had a high capacity to sorb heavy metals from solution mainly via an ion exchange process. The sorption of some heavy metals by the moss *Calymperes delessertii* Besch has been reported; the moss could sorb lead, copper and cadmium efficiently (Low and Lee 1987, 1991; Lee and Low 1989).

This study investigates the sorption characteristics of zinc by the moss, *Calymperes delessertii* Besch, and the possibility of using it to treat electroplating wastes.

MATERIALS AND METHODS

Sample Preparation

The collection and preparation of the moss, *Calymperes delessertii* Besch, have been described earlier (Lee *et al.* 1983). Air-dried samples of the moss in its natural condition were used in all the experiments.

A simulated wastewater prepared from A. R. grade anhydrous zinc chloride in 0.001 M sodium chloride solution was used in all the experiments studying the characteristics of zinc sorption by the moss. Sodium chloride solution was used to maintain constant ionic strength. Wastewater collected from an electroplating factory situated in an industrial park was used in the later experiments. The factory specializes in zinc plating and does not have any facility for wastewater treatment. The wastewater collected was alkaline and contained traces of nickel and iron in addition to zinc.

Contact Time Experiments

In all the contact time experiments, except where the effect of pH was investigated, 0.50 g of moss sample was shaken in 400 cm^3 of zinc solution. Various concentrations of zinc solution (250, 100 and 50 mg dm^{-3}) in 0.001 M sodium chloride were studied.

All batch experiments were performed in duplicates at room temperature (27°C). The zinc solution containing the preweighed moss was shaken in polyethylene bottles at 200 revolutions per minute (rpm) on a gyratory shaker. Aliquots of 1 cm^3 solutions were withdrawn at predetermined intervals.

In the study of the effect of pH, 0.20 g of moss was equilibrated with 100 cm^3 of 100 mg dm^{-3} zinc solution with pH ranging from 2 to 13 for four hours. The pH of the solution was adjusted by addition of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide.

Sorption Isotherm

In the study of the sorption capacity of the moss for zinc, 0.20 g samples of moss were shaken in 100 cm^3 of zinc solution for four hours. The concentrations of the solution were varied from 0.5 to 500 mg dm^{-3}.

Fixed Bed Study

In the flow studies, a vertical glass column of internal diameter 14 mm was used. The moss was packed to a height of 10, 15 and 20 cm, corresponding to 1.25 g, 1.88 g and 2.50 g of moss. The flow rates were controlled by means of a peristaltic pump attached to one end of the column. Zinc solutions of 50 mg dm^{-3} were passed through the column at flow rates of 20 to 50 cm^3 min^{-1}. Eluants were collected in 100 cm^3 and analysed for zinc. The experiments were repeated using wastewater containing 200 mg dm^{-3} of zinc and flow rates of 10 to 100 cm^3 min^{-1}.

Adsorption-Desorption Study

In the adsorption-desorption study, a glass column was packed with 2.50 g of moss to a height of 20 cm. One litre of 2.5 mg dm^{-3} zinc solution was passed through the column at a rate of 10 cm^3 min^{-1}.

The eluant was collected and checked for its zinc concentration. The column was then eluted with 1 M nitric acid. Twenty fractions of eluant with a volume of 10 cm^3 each were collected and analysed for zinc.

After the first adsorption-desorption process, the moss was washed free of acid by rinsing it with deionized water. The process was then repeated twice on the same column of moss.

Analysis of Zinc

The concentration of zinc in all the experiments was determined using a sequential scanning inductively coupled plasma atomic emission spectrometer (Labtest 710 - 2000).

RESULTS AND DISCUSSION

Zinc Content in Moss

The average concentration of zinc in the moss used in this study was 80 µg g^{-1} moss. The zinc content was low compared to that of mosses from contaminated areas, which was about 1914 µg g^{-1} moss (Lee *et al.*

1983). Zinc, together with other heavy metals in the atmosphere, was brought in contact with moss tissues in the form of precipitation and dust (Ruhling *et al.* 1968; Lazarus *et al.* 1970).

Contact Time Experiments

The reproducibility of the sorption capacity of the moss was demonstrated by equilibrating six replicates of 0.50 g moss in 100 cm^3 of 250 mg dm^3 zinc solution. A mean of 2.69×10^{-4} mol g^{-1} moss and relative standard deviation of 5.32% were obtained. Although no attempt was made to group the moss according to maturity, results from this reproducibility study suggest that sorption of zinc by moss was fairly uniform.

The rates of zinc sorption by the moss at various initial concentrations are shown in *Fig.1.* A very rapid initial uptake followed by a more gradual process after the first 5 minutes was observed. This could be due to a rapid ion-exchange process followed by chemisorption. This is a typical sorption pattern for most biological materials (Okieimen *et al.* 1985). The fractional uptake was inversely proportional to the initial concentration. Equilibrium was achieved at 30 minutes' contact time regardless of the initial concentration. This indicates the potential for rapid removal of zinc from solution.

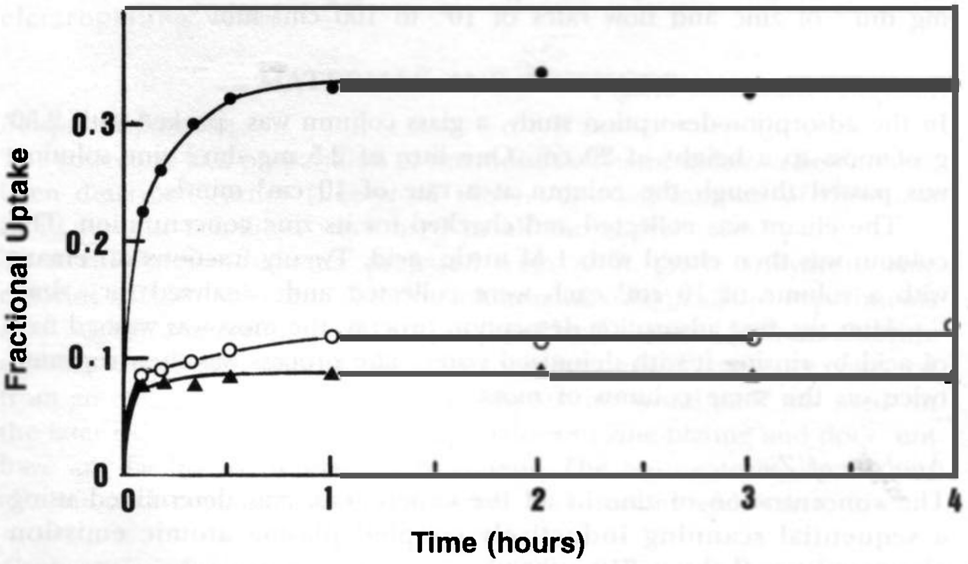

Fig. 1. Effect of initial zinc concentration on sorption.
● *50 mg* dm^{-3} ○ *100 mg* dm^{-3} ▲ *250 mg* dm^{-3}

The effect of pH on sorption of zinc is shown in *Fig. 2.* In the pH range of 2.45 to 4.70 there was an increase in sorption. As pH increases, the availability of sorption sites increases and hence the increase observed. At pH higher than 7, precipitation of zinc hydroxide started to occur.

A similar pattern was observed in the study of copper, lead and cadmium ion (Lee and Low 1989; Low and Lee 1991). Gjengedal and Steinnes (1990) found that at pH lower than 4 the amount of cadmium accumulated by the moss, *Hylocomium splendens*, decreased rapidly. This could be due to the hydrogen ions competing for the sorption sites. At pH 12 zinc hydroxide redissolved to form $[Zn(OH_4)]^{2-}$. There was, however, no uptake of zinc by the moss. As the pH of the electroplating wastewater collected was 12, it would be necessary to adjust the pH before experimentation using the wastewater.

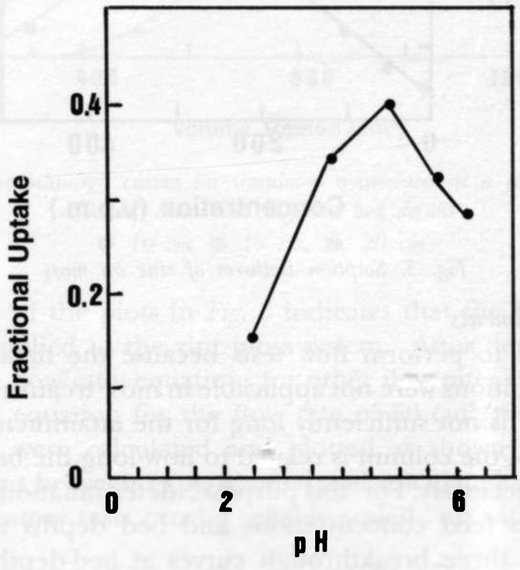

Fig. 2. Effect of pH on sorption

Sorption Isotherm

The results from sorption studies were fitted into a modified Langmuir adsorption isotherm as shown below :

$$C_i/N_i = 1/N^*b + C_iN_i/N^*$$

N_i is the number of moles sorbed per gram of moss at equilibrium concentration C_i. With this equation, the maximum number of moles of metal ion sorbed per gram of the moss (N^*) can be calculated. A plot of C_i/N_i against C_i is shown in *Fig. 3.* The linearity of the plot indicates the Langmuir isotherm can be applied successfully. The maximum sorption capacity is 21.50 mg or 329 μmol zinc g^{-1} moss.

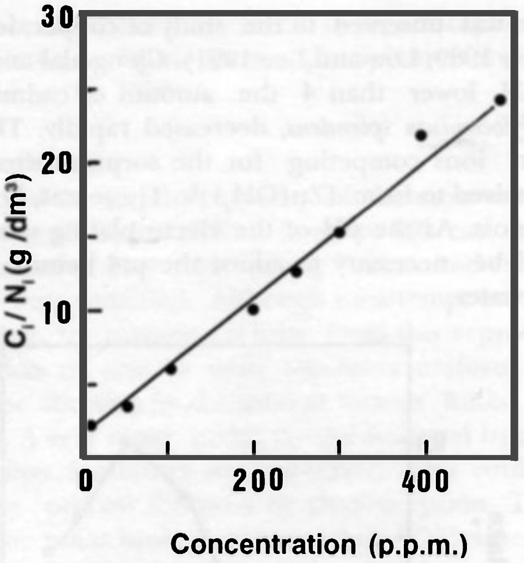

Fig. 3. Sorption isotherm of zinc on moss

Fixed Bed Experiments

There is a need to perform flow tests because the data obtained under equilibrium conditions were not applicable in most treatment systems where the contact time is not sufficiently long for the attainment of equilibrium. The usefulness of the column is related to how long the bed will last before regeneration is necessary. For this purpose, determination of breakthrough curves at various feed concentrations and bed depths is necessary.

Fig. 4 shows three breakthrough curves at bed-depths of 10, 15 and 20 cm and flow rates (μ) of 20 cm^3 min^{-1} with initial zinc concentration of 50 mg dm^{-3}. An arbitrary point of 50% breakthrough is chosen in this study as the level where effluent concentration is unacceptable. The time at which this occurred is labelled as $t_{1/2}$. Breakthrough curves with flow rates of 50 and 100 cm^3 min^{-1} were similar although breakthrough occurred faster.

The performance of a column can be evaluated using the bed depth service time (BDST) model (Hutchins 1973). The model states that bed depth and service time bear a linear relationship. The equation can be expressed as

$$t = ax + b$$

Plots of BDST ($t_{1/2}$) at breakthrough volume ($C/C_0 = 0.5$) against bed depth at different flow rates are shown in *Fig. 5*.

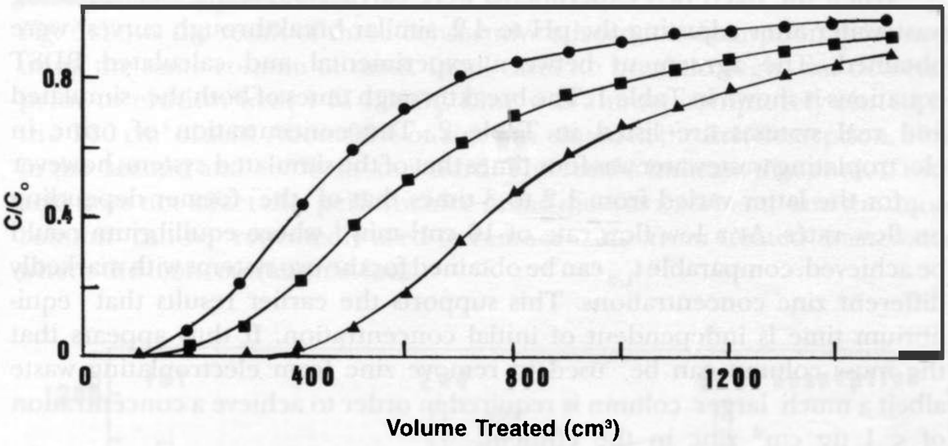

Fig. 4. Breakthrough curves for simulated wastewater at a flow rate of 20 cm³ /min and different bed depths
● *10 cm,* ■ *15 cm,* ▲ *20 cm*

The linearity of the plots in *Fig. 5* indicates that the BDST model can be successfully applied to the zinc-moss system. After developing a BDST equation for one flow rate, equations for other flow rates can be calculated. Using the BDST equation for the flow rate of 50 cm³/min, equations for other flow rates were calculated and plotted as shown in *Fig. 5*. There is good agreement between experimental and calculated values. Using this procedure, laboratory tests can be reliably scaled up without further test runs.

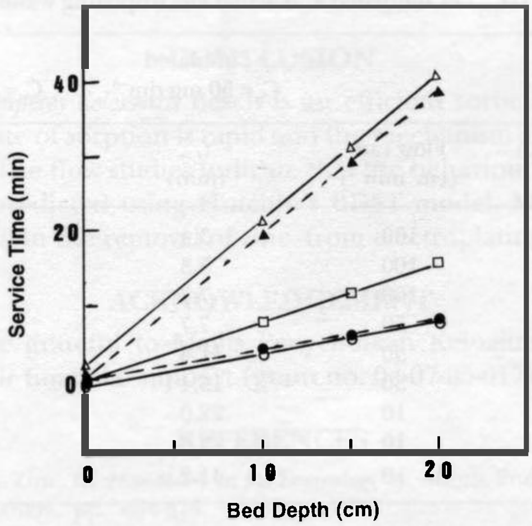

Fig. 5. BDST plots at 50% breakthrough for different flow rates
○, ● *100 cm³/min,* □ *50 cm³/min,* △, ▲ *20 cm³/min*
——— *Experimental values;* — — *calculated values*

When the fixed bed experiments were carried out using electroplating wastewater after adjusting the pH to 4.2, similar breakthrough curves were obtained. The agreement between experimental and calculated BDST equations is shown in Table 1. The breakthrough times of both the simulated and real systems are listed in Table 2. The concentration of zinc in electroplating wastewater was four times that of the simulated system; however $t_{1/2}$ for the latter varied from 1.2 to 3 times that of the former depending on flow rates. At a low flow rate of 10 $cm^3\ min^{-1}$ where equilibrium could be achieved, comparable $t_{1/2}$ can be obtained for the two systems with markedly different zinc concentrations. This supports the earlier results that equilibrium time is independent of initial concentration. It thus appears that the moss column can be used to remove zinc from electroplating waste albeit a much larger column is required in order to achieve a concentration of < 1 $\mu g\ cm^{-3}$ zinc in the effluent.

TABLE 1
Experimental and calculated BDST equations
for flow rates based on $\mu = 100\ cm^3\ min^{-1}$

$\mu (cm^3\ min^{-1})$	Experimental	Calculated
100	$t_{1/2} = 0.094x + 0.466$	-
50	$t_{1/2} = 0.194x + 1.026$	$t_{1/2} = 0.188x + 0.466$
10	$t_{1/2} = 1.224x + 5.303$	$t_{1/2} = 0.940x + 0.466$

TABLE 2
BDST ($t_{1/2}$) of simulated and actual electroplating wastewater

		Simulated $C_0 = 50\ mg\ dm^{-3}$	Actual $C_0 = 200\ mg\ dm^{-3}$
Bed depth (cm)	Flow rate ($cm^3 min^{-1}$)	$t_{1/2}$ (min)	$t_{1/2}$ (min)
10	100	3.4	1.4
15	100	5.3	1.8
20	100	7.7	2.4
10	50	7.7	3.1
15	50	11.4	3.8
20	50	15.4	5.0
10	10	22.0	17.5
15	10	29.8	23.8
20	10	41.2	29.7

Adsorption-Desorption Study

Fig. 6 shows the result of three consecutive adsorption-desorption processes using the same column of moss. In all cases no breakthrough was detected prior to elution with 1 M HNO_3. Zinc was almost completely eluted in the 100 cm^3 of acid. About 98% of zinc was eluted in the first desorption, 87% in the second and 103% in the third. The results indicate that elution with acid does not affect the performance of the moss as a sorbent, and the moss column can be repeatedly used to remove zinc from treated wastewater where the concentration is low.

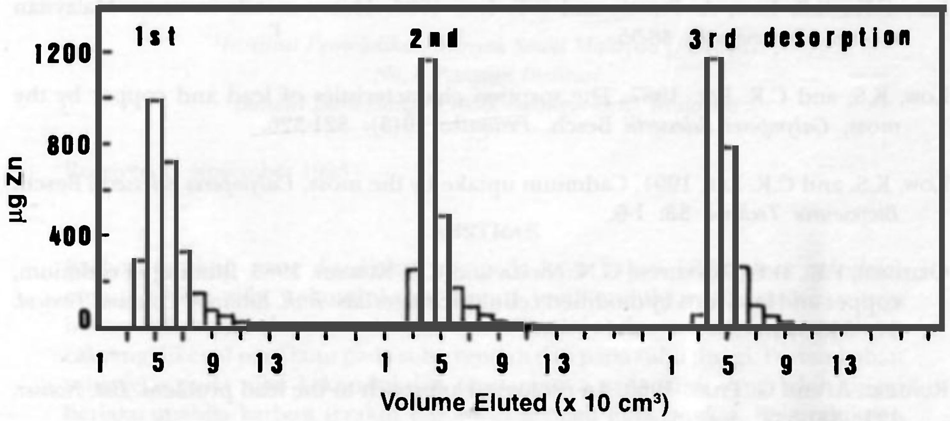

Fig. 6. Adsorption-desorption process of zinc in moss column

CONCLUSION

The moss, *Calymperes delessertii* Besch is an efficient sorbent for zinc from solution. The rate of sorption is rapid and the mechanism appears to involve ion exchange. The flow studies indicate that the behaviour of the zinc-moss system can be predicted using Hutchin's BDST model. Moss columns are potentially useful in the removal of zinc from electroplating wastewater.

ACKNOWLEDGEMENT

The authors are grateful to Majlis Penyelidikan Kemajuan Sains Negara, Malaysia for their financial support (grant no. 04-07-05-017).

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ISSN: 0128-7680
Pertanika J. Sci. & Technol. 2(2): 207-214 (1994)

Kajian Kekonduksian terhadap Karbon Teraktif daripada Kayu Bakau (*Rhizophora apiculata*)

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Received 11 November 1993

ABSTRAK

Karbon teraktif yang disediakan daripada kayu bakau (*Rhizophora apiculata*) menunjukkan sifat kekonduksian seperti semikonduktor. Kekonduksiannya bertambah secara eksponen dengan suhu. Terdapat dua mekanisme pengaliran cas yang dikenal pasti iaitu pada suhu rendah dan pada suhu tinggi. Pertambahan yang jelas pada nilai kekonduksian terutamanya pada suhu yang lebih tinggi berlaku apabila karbon teraktif didopkan dengan gula ringkas. Kekonduksian juga didapati bertambah dengan kepekatan gula.

ABSTRACT

Activated carbon prepared from mangrove wood (*Rhizophora apiculata*) shows conduction behaviour similar to that of semiconductors. The conductivity increases exponentially with the temperature. Two types of charge transfer mechanism are identified, i. e. at low and high temperature. A significant increase in the conductivity was observed especially at high temperature, when the carbon was doped with simple sugar. The conductivity was also found to increase with the sugar concentration.

Katakunci: karbon teraktif, kayu bakau, kekonduksi

PENDAHULUAN

Karbon teraktif telah banyak digunakan dalam industri dengan mengeksploitasikan sifat jerapan bahan tersebut. Bagi karbon teraktif yang disediakan daripada sumber semula jadi, kuasa jerapan ini dikaitkan dengan luas permukaannya yang tinggi melebihi 100 m^2/g dan kehadiran liang-liang seni yang banyak dengan pelbagai saiz (Dubinin 1966; Mattson dan Mark 1971). Kajian terhadap sifat karbon teraktif sebagai bahan penjerap telah banyak dilakukan. Walau bagaimanapun kajian terhadap sifat elektrik karbon teraktif masih kurang mendapat perhatian.

Karbon teraktif dapat dikelaskan sebagai semikonduktor amorfus berdasarkan sifat kekonduksiannya. Kajian kekonduksian ke atas karbon teraktif daripada tempurung kelapa sebelum ini menunjukkan bahawa pembawa cas utama adalah lubang positif pada suhu kurang dari 385 K (Daud *et al.* 1990). Atas daripada suhu ini pembawa cas utama adalah elektron. Kekonduksian dalam karbon teraktif mungkin berpunca daripada kehadiran logam surih yang diperlukan oleh tumbuhan atau disebabkan oleh penarikan elektron daripada sistem-π gelang grafit. Mekanisme pengangkutan cas pula berbeza-beza pada beberapa julat suhu yang berlainan.

Kajian kekonduksian karbon teraktif yang disediakan daripada kayu bakau yang mana pencirian beberapa sifat kimia dan fiziknya yang lain telah pun dilakukan (Zulkarnain *et al.* 1993) akan dibincangkan. Perkaitan di antara kekonduksian karbon teraktif ini dengan kandungan logam surih yang diperolehi daripada data analisis pengaktifan neutron juga akan dibincangkan. Selain daripada itu kesan penambahan bendasing organik kepada karbon teraktif juga akan dikaji.

BAHAN DAN KAEDAH

Kepingan karbon teraktif kayu bakau disediakan dengan kaedah persulingan memusnah (British Patent Office 1984) pada suhu dan tekanan optimum seperti yang dinyatakan oleh Zulkarnain *et al.* (1993), bagi menghasilkan luas permukaan yang terbaik. Kepingan tersebut kemudiannya dipotong dan diasah menjadi cakra-cakra berbentuk bulat dengan garis pusat 10 mm dan ketebalan 1.3 mm.

Pengukuran kekonduksian dilakukan di dalam tiub kaca yang divakumkan. Cakra karbon teraktif dikepit di antara dua plat selari keluli tahan karat. Nilai kekonduksian dibaca pada Wayne Kerr Autobalance Universal Bridge B642. Pemanasan dilakukan dengan menggunakan pita pemanas yang dibalut pada tiub kaca dan dikawal dengan menggunakan pengubah voltan.

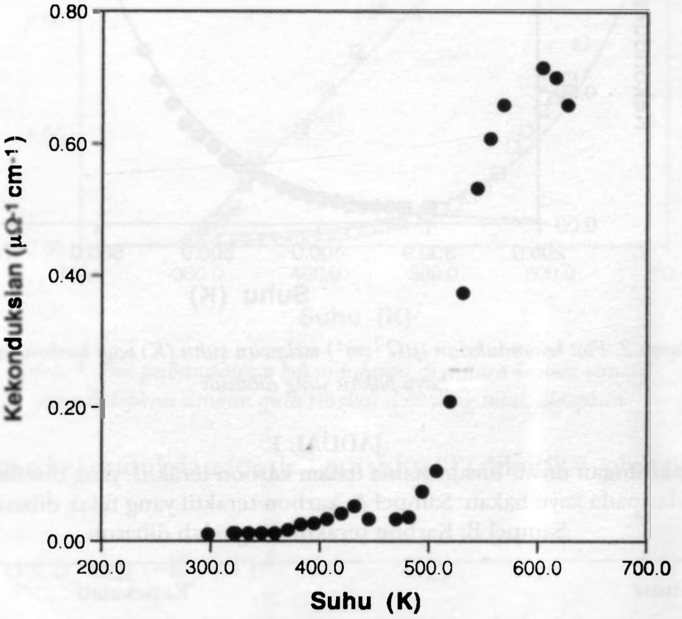
Untuk sampel yang perlu dibasuh, setiap kali pembasuhan, sampel cakra karbon direfluks dalam 1 M asid hidroklorik diikuti dengan air suling selama satu minggu.

Proses pendopan dilakukan dengan merendamkan cakra karbon teraktif di dalam larutan gula selama tiga hari. Cakra tersebut kemudiannya dikeringkan di dalam ketuhar pada suhu 110°C sebelum pengukuran kekonduksian dijalankan.

Penentuan kandungan unsur surih tak organik dilakukan dengan kaedah analisis pengaktifan neutron. Sampel karbon teraktif yang telah dibasuh dihantar ke Unit Tenaga Nuklear untuk tujuan tersebut.

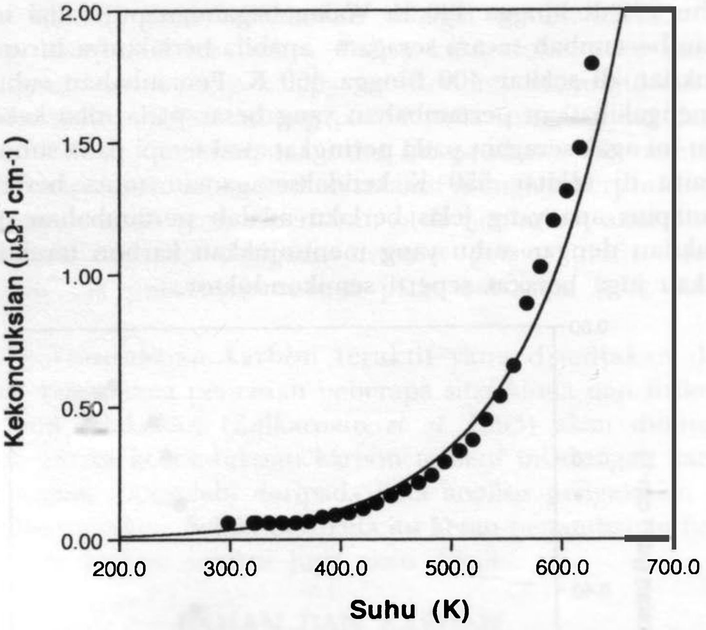
KEPUTUSAN DAN PERBINCANGAN

Plot kekonduksian karbon teraktif tanpa pra-rawatan terhadap suhu di dalam *Rajah 1* menunjukkan kekonduksian berada pada nilai yang rendah pada julat suhu 290 K hingga 490 K. Walau bagaimanapun nilai ini tidaklah tetap atau bertambah secara seragam apabila berlakunya turun naik nilai kekonduksian di sekitar 400 hingga 460 K. Penambahan suhu melebihi 490 K mengakibatkan pertambahan yang besar pada nilai kekonduksian. Kenaikan ini agak seragam pada peringkat awal tetapi pada suhu yang agak tinggi iaitu di sekitar 550 K ketidakseragaman mula berlaku. Walau bagaimanapun apa yang jelas berlaku adalah pertambahan dalam nilai kekonduksian dengan suhu yang menunjukkan karbon teraktif daripada kayu bakau juga bersifat seperti semikonduktor.



Rajah 1. Plot kekonduksian ($\mu\Omega^{-1}cm^{-1}$) melawan suhu (K) bagi karbon teraktif kayu bakau yang tidak dibasuh

Pertambahan yang tidak seragam dalam nilai kekonduksian bolehlah dihubungkan dengan kehadiran unsur surih dalam karbon teraktif tersebut, seperti yang ditunjukkan di dalam Jadual 1. Sampel A adalah karbon teraktif yang tidak dibasuh. Pembasuhan juga dapat mengurangkan kandungan unsur surih (sampel B) seperti yang telah dijelaskan oleh Zulkarnain *et al.* (1993). Kehadiran unsur ini mungkin dapat memberikan sumbangan sebagai pembawa cas kepada karbon teraktif disamping pembawa cas dari sistem-π gelang grafit. Fenomena ini terbukti apabila pengukuran kekonduksian dilakukan ke atas karbon teraktif yang telah dibasuh (*Rajah 2*). Gangguan pembawa cas unsur surih telah dapat dihapuskan apabila satu lengkuk kekonduksian melawan suhu yang lebih baik diperolehi. Ia menunjukkan bahawa nilai kekonduksian bertambah dengan suhu. Peningkatan ini lebih ketara pada suhu yang lebih tinggi.

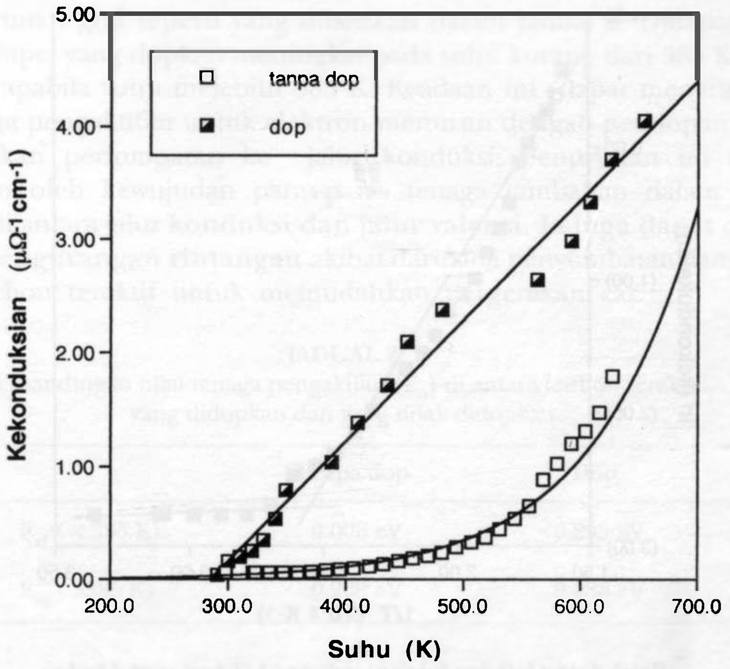


Rajah 2. Plot kekonduksian ($\mu\Omega^{-1}cm^{-1}$) melawan suhu (K) bagi karbon teraktif kayu bakau yang dibasuh

JADUAL 1
Kandungan unsur-unsur utama dalam karbon teraktif yang disediakan daripada kayu bakau. Sampel A: karbon teraktif yang tidak dibasuh. Sampel B: Karbon teraktif yang telah dibasuh

Unsur	Kepekatan	
	Sampel A	Sampel B
Na(%)	0.299 ± 0.011	0.067 ± 0.003
K (%)	0.155 ± 0.003	0.020 ± 0.002
Ca(%)	1.15 ± 0.02	0.33 ± 0.04
Cl(%)	0.026 ± 0.004	1.208 ± 0.013
Mn(p.p.m.)	38 ± 2	50 ± 2

Rajah 3 pula menunjukkan perbandingan kekonduksian bagi karbon teraktif yang didopkan dengan gula ringkas dan yang tidak didopkan. Pendopan didapati telah meningkatkan nilai kekonduksian karbon teraktif dengan banyaknya. Pertambahan tersebut seolah-olah berlaku secara linear dengan pertambahan suhu.



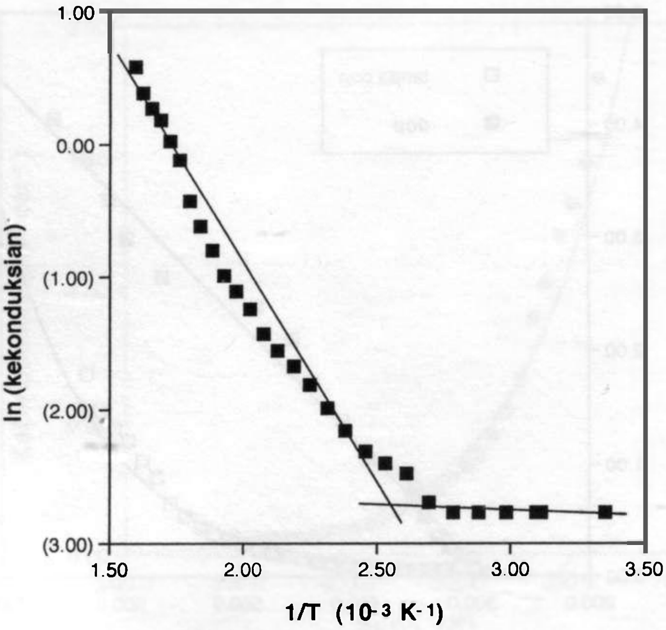
Rajah 3. Plot perbandingan kekonduksian di antara karbon teraktif yang didopkan dengan gula ringkas dan yang tidak didopkan

Hubungan kekonduksian (σ) dengan suhu (T) diberikan oleh persamaan berikut:-

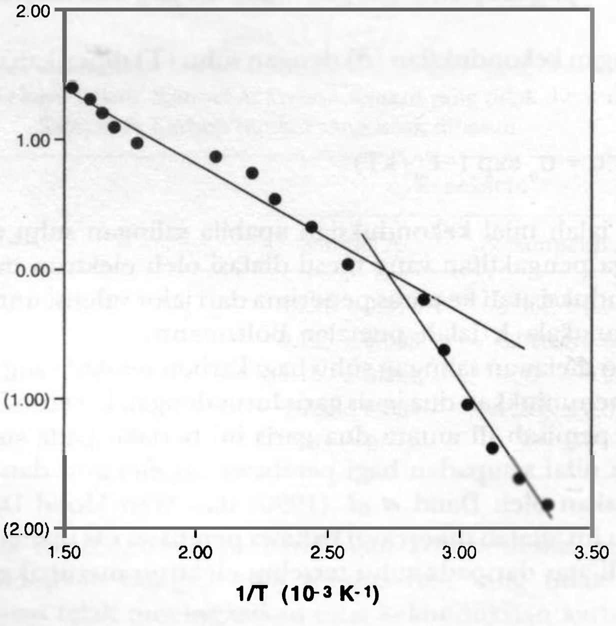
$$\sigma = \sigma_o \exp(-E_\alpha/kT) \qquad (1)$$

dengan σ_o ialah nilai kekonduksian apabila salingan suhu adalah sifar. E_α ialah tenaga pengaktifan yang mesti diatasi oleh elektron untuk melompat ke jalur konduksi atau ke paras penerima dari jalur valensi untuk membentuk lubang. Manakala k ialah pemalar Boltzmann.

Plot ln σ melawan salingan suhu bagi karbon teraktif yang tidak didopkan (*Rajah 4*) menunjukkan dua jenis garis lurus dengan kecerunan yang berbeza. Sempadan pemisah di antara dua garis ini berlaku pada suhu 370 K yang merupakan nilai sempadan bagi pembawa cas elektron dan lubang seperti yang dijelaskan oleh Daud *et al.* (1990) dan Wan Mohd Daud (1991). Di bawah suhu ini adalah dipercayai bahawa pembawa cas utama adalah lubang, manakala di atas daripada suhu tersebut elektron merupakan pembawa cas utama.



Rajah 4. Plot ln(kekonduksian) melawan 1/T bagi sampel karbon teraktif kayu bakau yang tidak didopkan



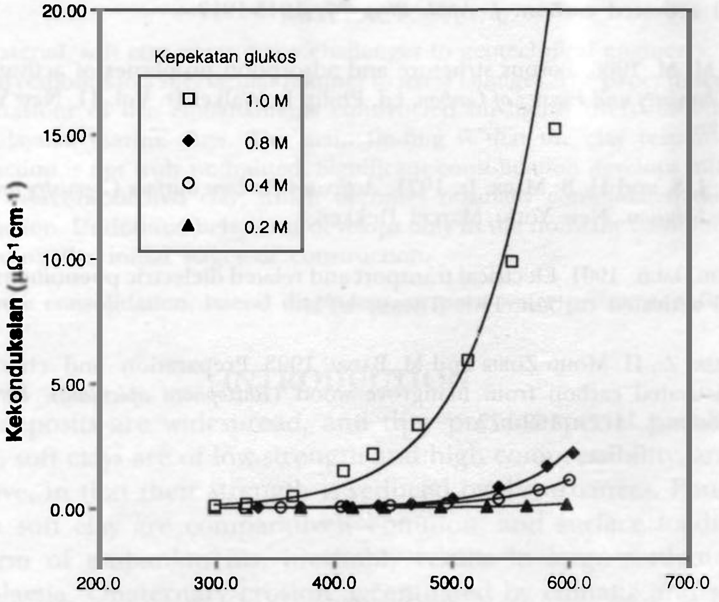
Rajah 5. Plot ln(kekonduksian) melawan 1/T bagi sampel karbon teraktif kayu bakau yang didopkan dengan gula ringkas

Plot yang sama bagi karbon teraktif yang didopkan dengan gula ringkas (*Rajah 5*) juga menunjukkan sempadan yang sama. Nilai E_α dapat dikira dari kecerunan graf seperti yang diberikan dalam Jadual 2. Didapati nilai E_α bagi sampel yang dopkan meningkat pada suhu kurang dari 385 K tetapi menurun apabila suhu melebihi 385 K. Keadaan ini dapat menerangkan nilai tenaga pengaktifan untuk elektron menurun dengan pendopan untuk memudahkan perlompatan ke jalur konduksi. Penurunan ini adalah disebabkan oleh kewujudan paras-paras tenaga tambahan dalam ruang larangan di antara jalur konduksi dan jalur valensi. Ia juga dapat dilihat sebagai pengurangan rintangan akibat daripada penyumbatan liang-liang dalam karbon teraktif untuk memudahkan pergerakan cas.

JADUAL 2
Perbandingan nilai tenaga pengakifan (E_α) di antara karbon teraktif yang didopkan dan yang tidak didopkan

	Tanpa dop	Dop
$E_{\alpha1}$ (< 385 K)	0.006 eV	0.293 eV
$E_{\alpha2}$ (>385 K)	0.268 eV	0.088 eV

Penambahan nilai E_α pada suhu kurang dari 385 K untuk karbon teraktif yang didopkan pula membuktikan bahawa pada tahap ini lubang memainkan peranan sebagai pembawa cas utama.



Rajah 6. Plot kekonduksian ($\mu\Omega^{-1}cm^{-1}$) melawan suhu bagi karbon teraktif kayu bakau yang direndam selama dua hari dalam beberapa kepekatan glukos

Rajah 6 pula menunjukkan bahawa peningkatan nilai kekonduksian bergantung kepada kepekatan gula di dalam larutan semasa proses pendopan. Semakin tinggi kepekatan gula akan meninggikan juga nilai kekonduksian. Walau bagaimanapun kajian hubungan kepekatan, tempoh rendaman dan kekonduksian masih dalam kajian.

KESIMPULAN

Karbon teraktif daripada kayu bakau didapati bersifat seperti semikonduktor amorfus. Nilai kekonduksiannya bertambah dengan suhu dan dapat ditingkatkan melalui pendopan. Di samping itu kekonduksian juga bergantung kepada kuantiti bahan pendopan yang terdapat di dalam karbon teraktif. Proses pendopan ini didapati telah dapat mengurangkan nilai tenaga pengaktifan (E_a) bagi elektron.

PENGHARGAAN

Kami ingin merakamkan setinggi-tinggi penghargaan kepada MPKSN kerana membiayai projek ini dibawah gran IRPA 2-07-05-009-J01 dan Unit Tenaga Nuklear kerana memberikan perkhidmatan analisis pengaktifan neutron.

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ISSN: 0128-7680
Pertanika J. Sci. & Technol. 2(2): 215-235 (1994)

Behaviour of Soft Clay Foundation beneath an Embankment

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Received 18 October 1993

ABSTRAK

Sebagai bahan tanah liat lembut memberi banyak cabaran kepada jurutera-jurutera geoteknik. Bahan ini bertindakbalas dalam cara yang menakjubkan kepada perubahan tegasan. Di dalam rencana ini kelakuan lima buah benteng yang dibina di atas tanah liat lembut diperihalkan. Tanah-tanah ini merupakan tanah liat marin Malaysia yang terkukuh lebih sedikit. Penemuan utama yang didapati ialah tindakbalas tanah liat semasa pembinaan tidaklah tak bersalir sepenuhnya. Sedikit pengukuhan berlaku di dalam tanah liat terkukuh lebih di peringkat awal pembinaan. Tanah ini selanjutnya menjadi terkukuh normal semasa pembinaan diteruskan. Kelakuan tak bersalir hanya berlaku apabila tanah liat menjadi berkukuh normal.

ABSTRACT

As a material, soft clay poses many challenges to geotechnical engineers. The material responds in a spectacular manner to stress changes. The paper describes the behaviour of five embankments constructed on lightly overconsolidated soft Malaysian marine clays. The main finding is that the clay response to construction is not truly undrained. Significant consolidation develops initially in the overconsolidated clay, which becomes normally consolidated during construction. Undrained behaviour develops only in the normally consolidated clay during the initial stages of construction.

Keywords: consolidation, lateral displacement, pore water pressure, soft clay

INTRODUCTION

Soft clay deposits are widespread, and they present special problems. By definition, soft clays are of low strength and high compressibility, and many are sensitive, in that their strength is reduced by disturbances. Foundation failures in soft clay are comparatively common, and surface loading, e.g. in the form of embankments, inevitably results in large settlements.

In Malaysia, Quaternary erosion accentuated by climatic and sea level changes has produced widespread thick deposits of soft clays in the coastal areas and major river valleys, of varying thickness, ranging from 5 m to 30 m. Reviews of the basic and engineering properties of some of these deposits have been published by Ting *et al.* (1987) and Abdullah and Chandra

(1987). With the development of communication networks due to the increasing pace of industrialization and urbanization, the design and construction of embankments on soft clays have become problems of major importance to geotechnical engineers. The capacity to design an embankment economically on a clay foundation and to predict its behaviour are thus of great interest to the profession.

As a material, soft clay poses abundant engineering challenges. The designer must often use very low safety factors, and the decisions he takes can have large economic consequences for the project.

The usual methods for the design of embankments on soft clays have been developed from simplified assumptions and empirical approaches. The material responds in such a spectacular manner to stress changes that it offers the engineer-scientist special opportunities to evaluate the theories of soil mechanics. This evaluation process has been particularly facilitated by a number of carefully planned full-scale field trials which have been carried out in recent years, and by a series of well-documented case histories. Among major reviews of design practices are those made by Bjerrum (1972), and Tavenas and Leroueil (1980).

The present paper describes the behaviour of five embankments constructed on soft Malaysian clays. The first two embankments (designated embankment 1 and 2) were nominally 3 m and 6 m high, constructed on top of about 20 m soft marine clay. The third, fourth and fifth embankments (designated embankment 3, 4 and 5) were 2.0 m, 2.5 m and 3.5 m high constructed on top of about 14 m - 20 m of very soft to soft silty/sandy clay. All these embankments were instrumented with settlement markers, piezometers and inclinometers.

LOCATION OF SITES AND PROPERTIES OF THE GROUND

Embankments 1 and 2 are trial embankments constructed by the Malaysian Highway Authority in 1988, in the southern state of Johor, Peninsular Malaysia. The subsoil profile comprises about 20 m of a soft to very soft marine clay, underlain by a layer of loose to dense, medium to coarse sand, with SPT values of 6 - 50. The natural water content of the soft clay layer varies from 50 - 120%, liquid limit 40 to 80% and plastic limit 20 to 50%. Traces of sea shells indicate a marine origin. A summary of the geotechnical properties of the clay layer is given in *Fig. 1.* The undrained shear strength (Su) obtained from the vane test showed an almost linear increase of strength below a surface crust with an average strength of 9 kPa at depth 1 m, increasing to 36 kPa at depth 17 m, or 8 - 36 kPa if corrected with Bjerrum (1972) correction factor for anisotropy and shear rate. The Su/σ c ratio (σ c = effective preconsolidation pressure) is in the range of 0.21 - 0.29, the higher Su/σ c ratio for the upper more plastic clay. This is in reasonable agreement with correlations obtained from other sites of similar soft clays, e.g. Su = (0.24 ± 0.04) σ c (Larrson

1980); $Su = (0.24 \pm 0.04)\ \sigma c\ OCR^{0.8}$ (Jamiolkowski *et al.* 1979); $Su = (0.22 \pm 0.02)\ \sigma c$ (Ladd 1981). The above trend of $Su/\sigma c$ increase with increase in soil plasticity has also been observed at other sites by Larrson (1980) and Balasubramaniam *et al.* (1985). The clays are also known to be fairly sensitive, with a sensitivity ratio in the range of 3 to 6. Ratios of Eu/Su with Eu (undrained modulus) obtained from the laboratory were found to vary from 230 - 455, apparently higher than data from other field sites of similar clays, e.g. Eu/Su = 190 (Poulus *et al.* 1989). However, other published literature also indicates a substantial variation of undrained strength and stiffness ratio, e.g. Eu/Su varying from < 200 to 2000 has been reported by Foott and Ladd (1981), depending on stress level and soil type. Results obtained from the oedometer tests indicate that the clays are slightly overconsolidated but highly compressible. Values of cv are

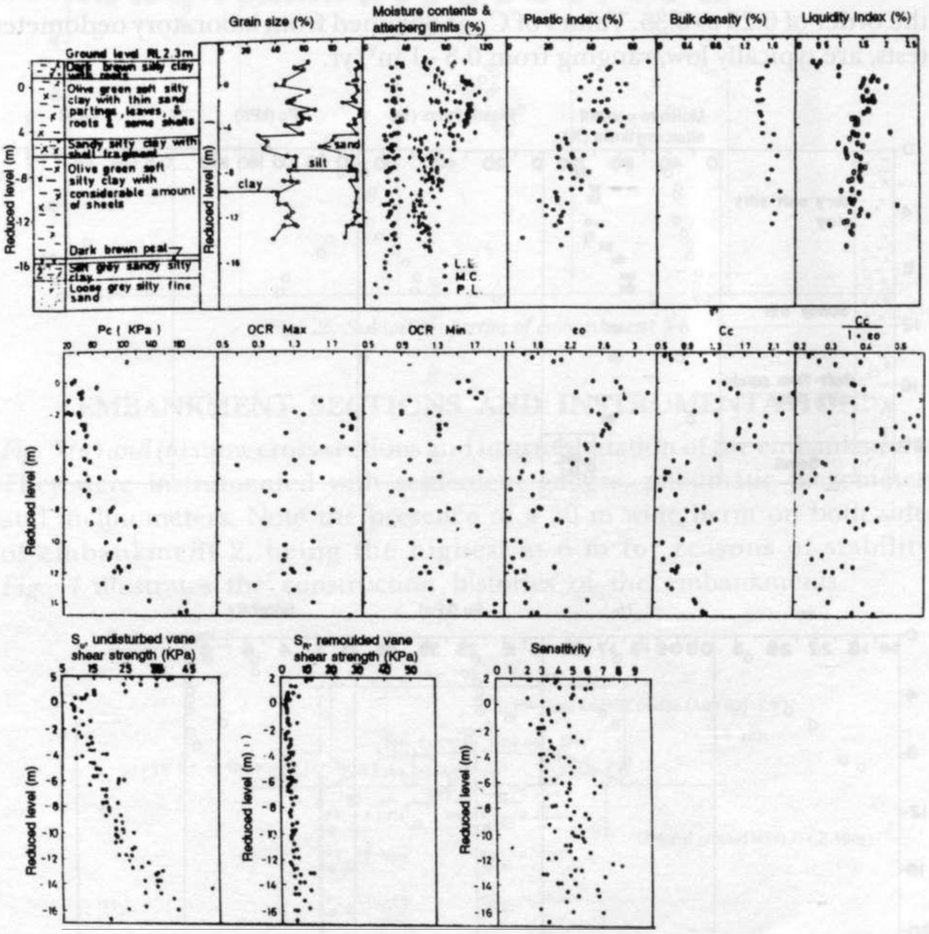


Fig. 1. Subsoil properties of embankments 1 and 2

typical low, ranging from 1 - 10 m^2/yr, and scattered, and Cc values are in the range of 0.6 - 1. The soil permeabilities (k_v k_h) are generally less than 5×10^{9} m/s, with a clay fraction of the order of 50% and kaolinite as the dominant mineral present.

Embankments 3, 4 and 5 are part of the North-South Expressway, constructed in 1992-93, in the northern state of Penang, Peninsular Malaysia. The subsoil profile comprises a 14 m to 20 m thick layer of soft to very soft silty/sandy clay with thin lenses of sand and silt, and underlain by a layer of loose to dense sand. The liquid limit of the soft clay layer varies from 50% to 110%, with natural water content close to the liquid limit, and plastic limit in the range of 20% to 60%. A summary of the geotechnical properties of the clay layer is given in *Fig. 2 (a) and (b)*. In general, the undrained shear strength of the clay obtained from the vane test showed an increase of strength with depth, below a surface crust. The clays are lightly overconsolidated with OCR values in the range of 1.1 to 2.1 but fairly compressible. The Su/σc ratio is in the order of 0.25 to 0.35. Values of C_v, as obtained from laboratory oedometer tests, are typically low, ranging from 0.3 - 1 m^2/yr.

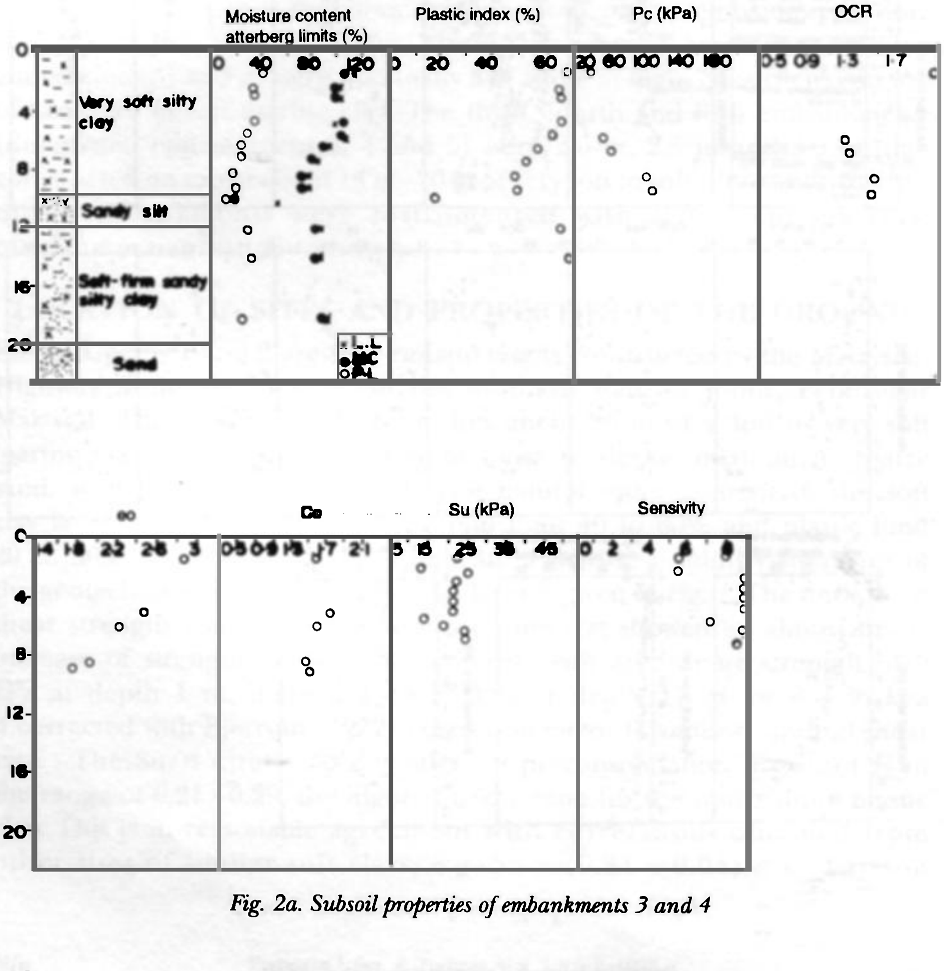


Fig. 2a. Subsoil properties of embankments 3 and 4

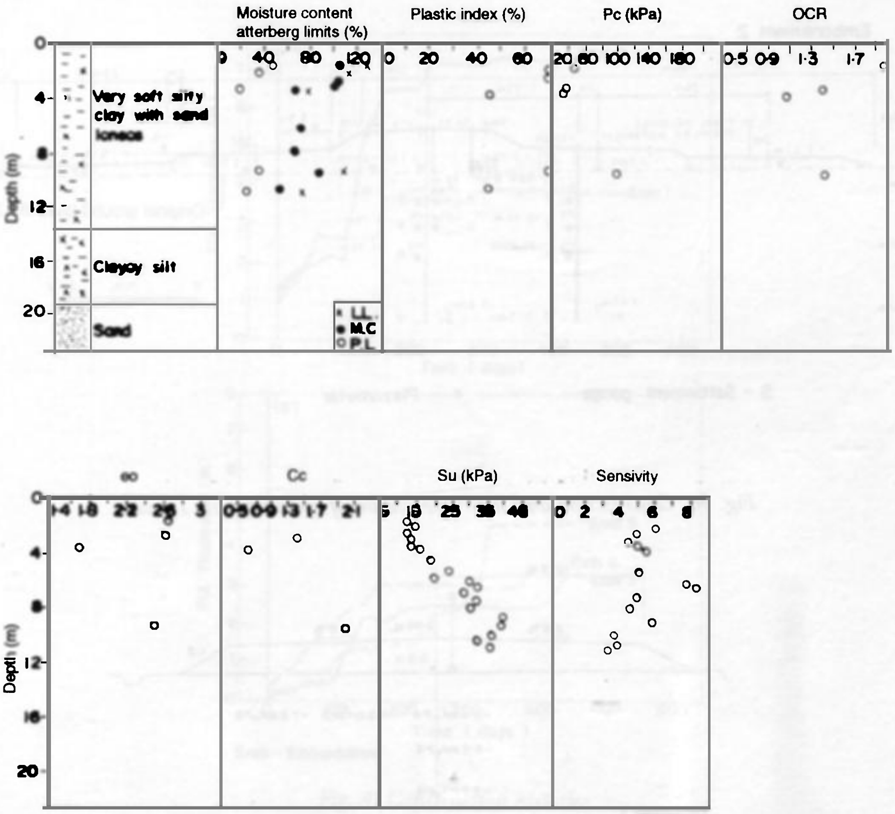
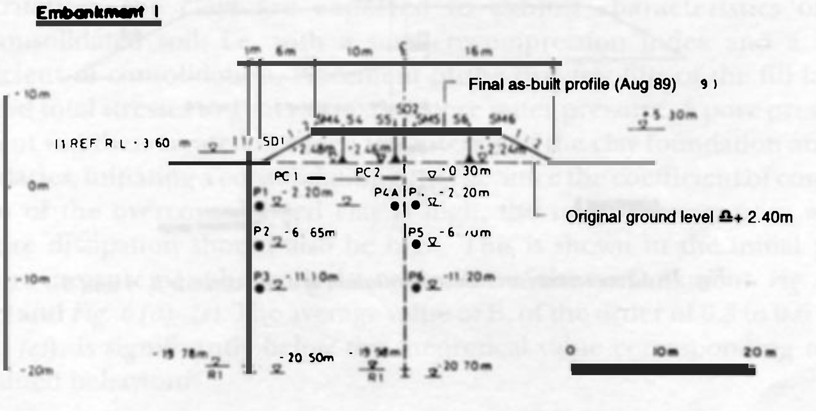


Fig. 2b. Subsoil properties of embankment 5

EMBANKMENT SECTIONS AND INSTRUMENTATION

Fig. 3 (a) and (b) show cross-sections and instrumentation of the embankments. They were instrumented with settlement gauges, pneumatic piezometers and inclinometers. Note the presence of a 50 m wide berm on both sides of embankment 2, being the highest at 6 m for reasons of stability. *Fig. 4* illustrates the construction histories of the embankments.



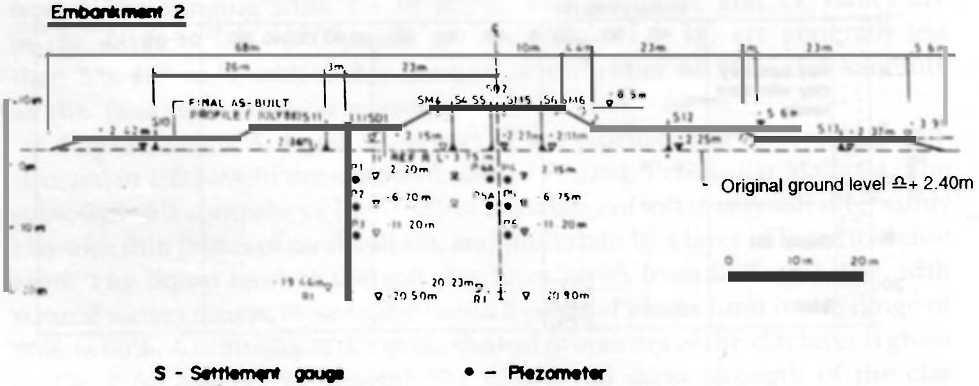


Fig. 3a. Cross-section and instrumentation of embankments 1 and 2

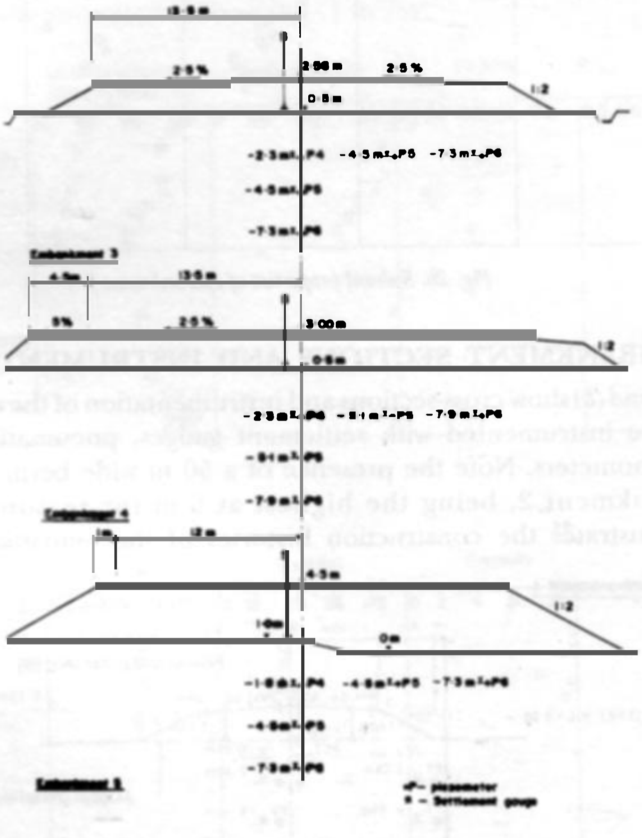


Fig. 3b. Cross-section and instrumentation of embankments 3, 4 and 5

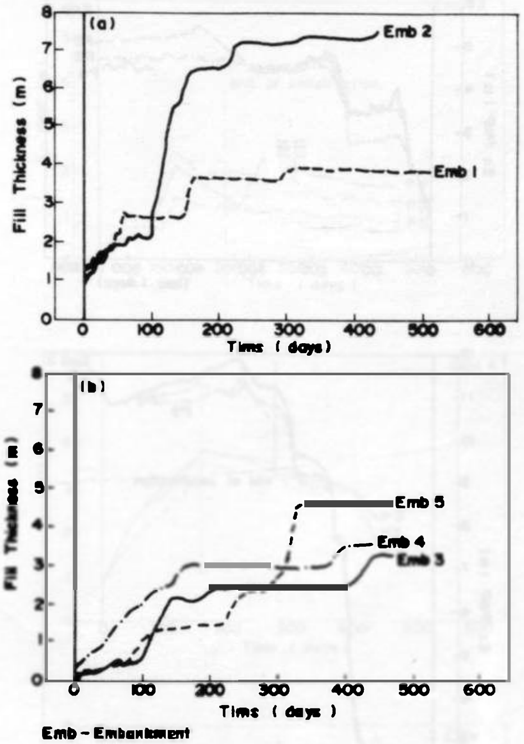


Fig. 4. Construction histories

OBSERVED BEHAVIOUR OF SOFT CLAY FOUNDATIONS

At the Beginning of Construction

Surface desiccation, groundwater fluctuation or aging nearly always causes soft clays to exhibit light overconsolidation, although they are commonly normally consolidated (Bjerrum 1967). For the subsoil of embankments 1 and 2, the values of apparent OCR estimated on conventional oedometer tests were in the range of 1.1 to 1.7. A similar range of apparent OCR was also found for the subsoil of embankments 3, 4 and 5. At the initial stage of embankment construction, the clays are expected to exhibit characteristics of an overconsolidated soil; i.e. with a small recompression index and a high coefficient of consolidation. Placement of the first few lifts of the fill layers induced total stresses to generate excess pore water pressure. A pore pressure gradient was then created between the interior of the clay foundation and its boundaries, initiating a consolidation process. Since the coefficient of consolidation of the overconsolidated clay is high, the rate of excess pore water pressure dissipation should also be high. This is shown in the initial pore pressure measurement beneath the centreline of the embankment, *Fig. 5 (a) and (c)* and *Fig. 6 (a) - (e)*. The average value of B, of the order of 0.3 to 0.6 (*Fig. 6 (a) - (e)*), is significantly below the theoretical value corresponding to an undrained behaviour.

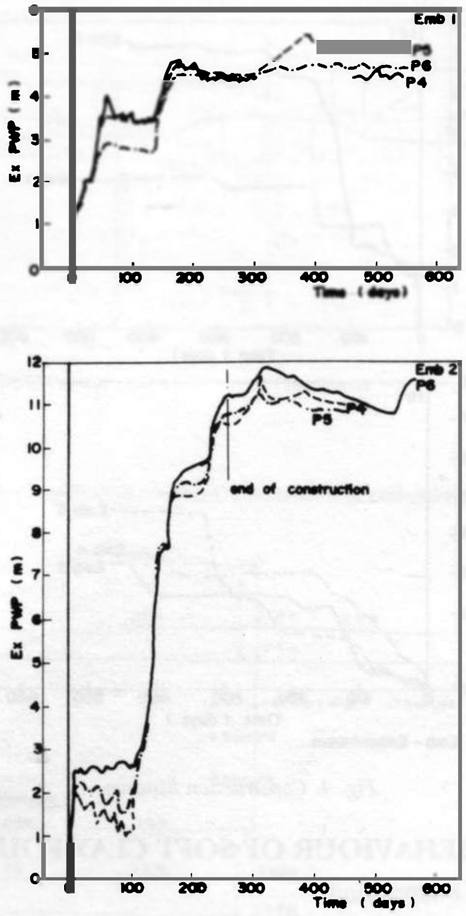


Fig. 5a. Excess pore water pressures - centreline piezometers (embankments 1 and 2)

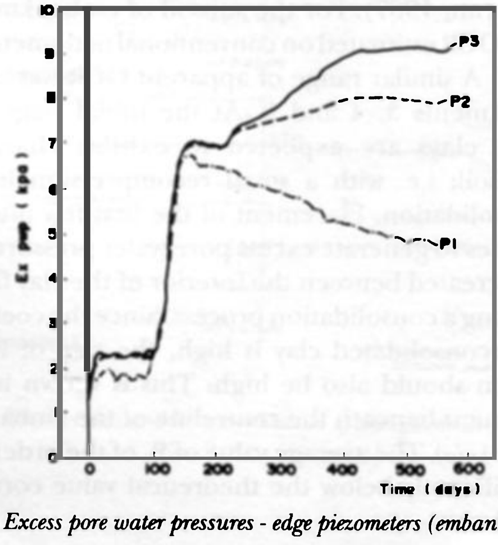


Fig. 5b. Excess pore water pressures - edge piezometers (embankment 2)

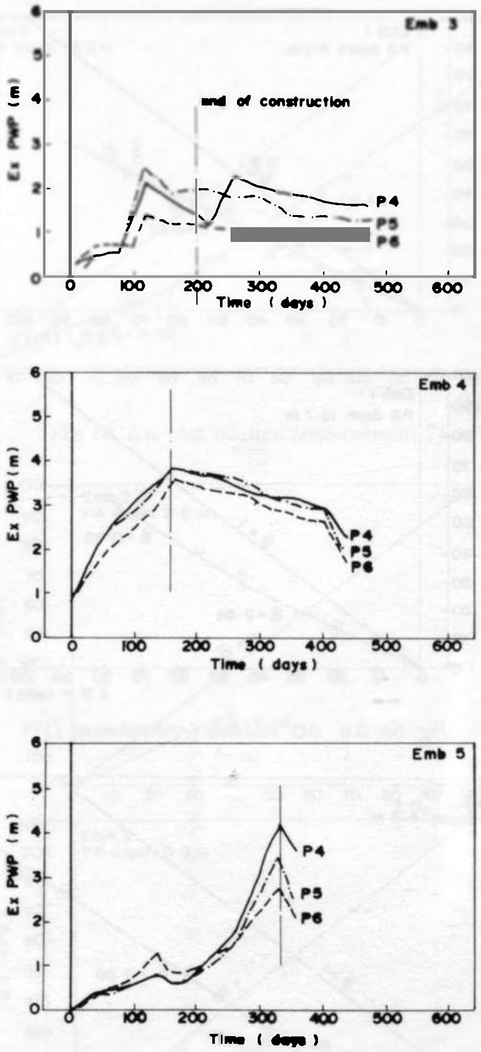
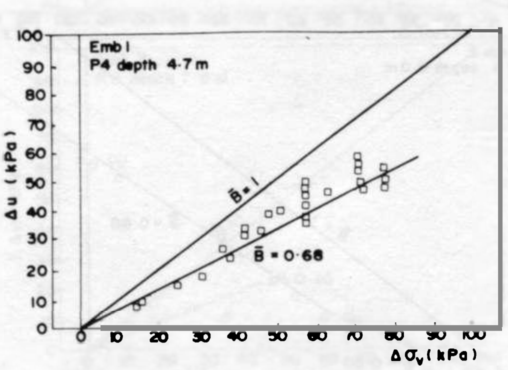


Fig. 5c. Excess pore water pressures - centreline piezometers (embankments 3, 4 and 5)



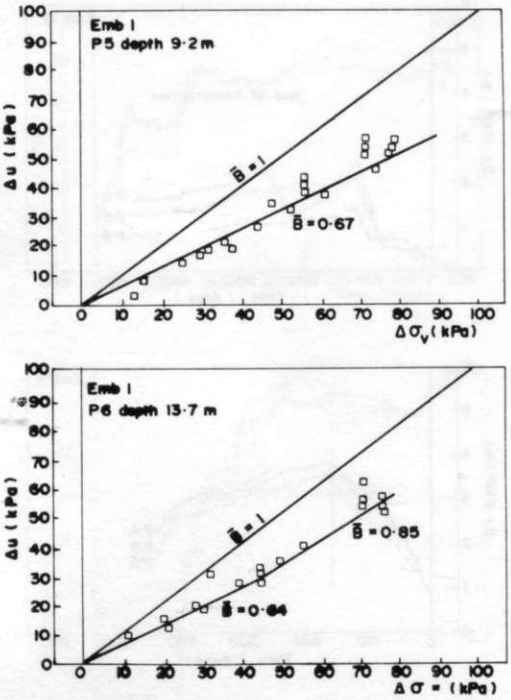
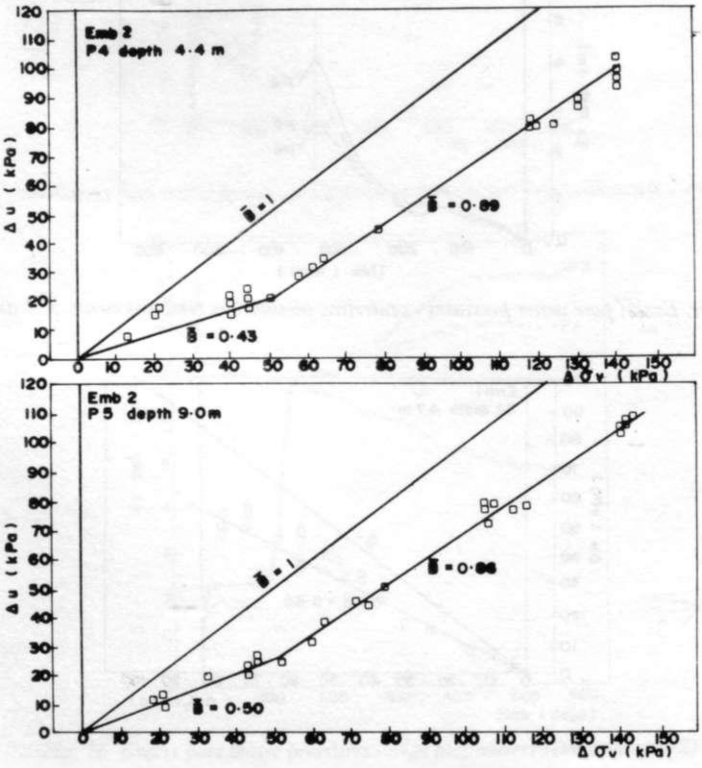


Fig. 6a. Δu - Δσ *relation (embankment 1)*



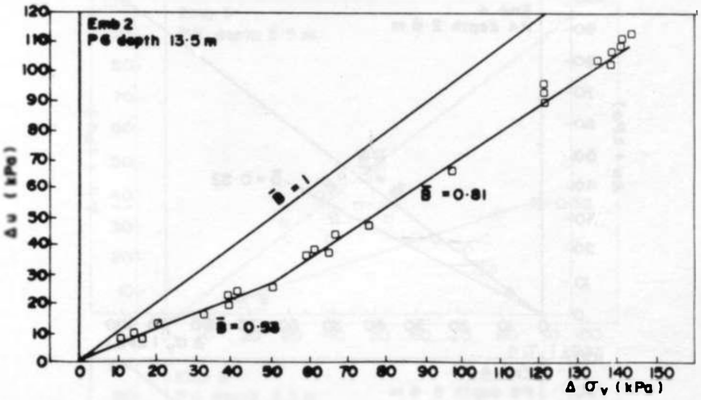


Fig. 6b. Δu - $\Delta\sigma$ *relation (embankment 2)*

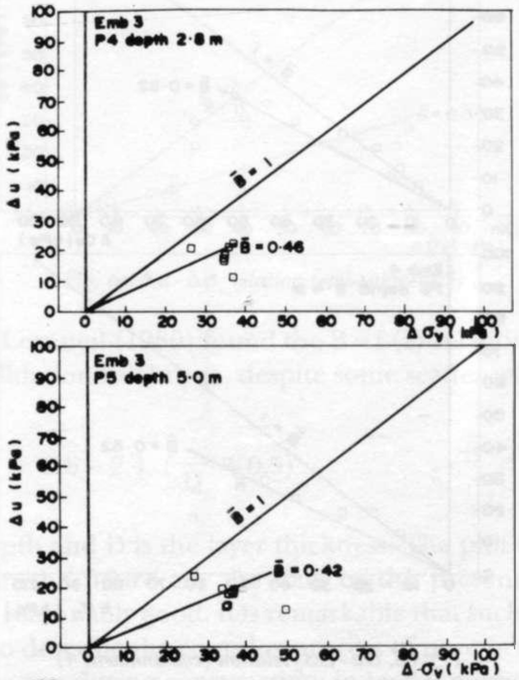


Fig. 6c. Δu - $\Delta\sigma_v$ *relation (embankment 3)*

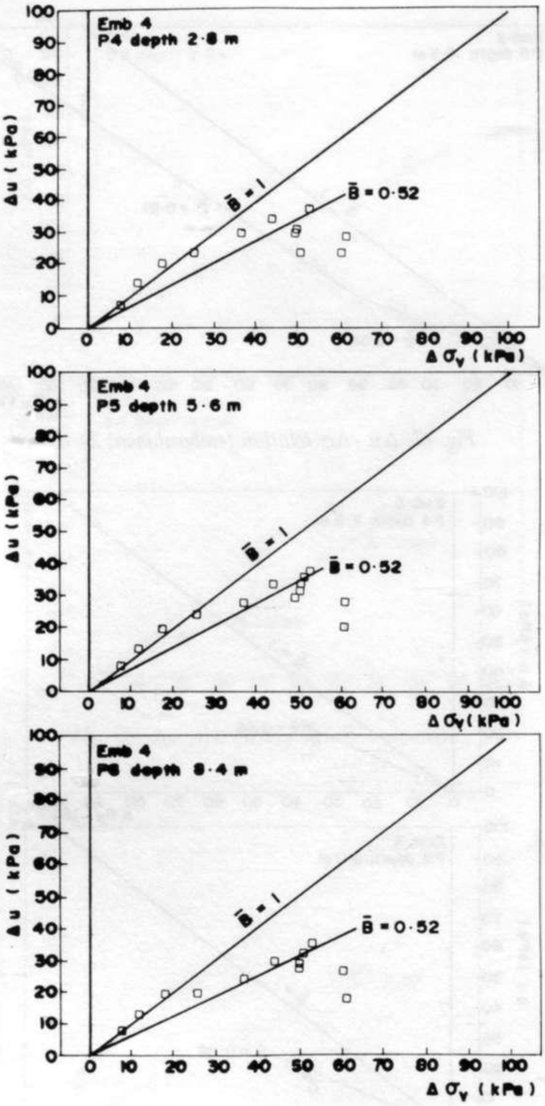
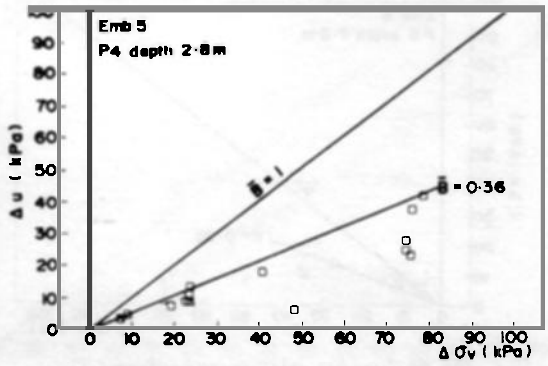


Fig. 6d. $\Delta u - \Delta\sigma_v$ *relation (embankment 4)*



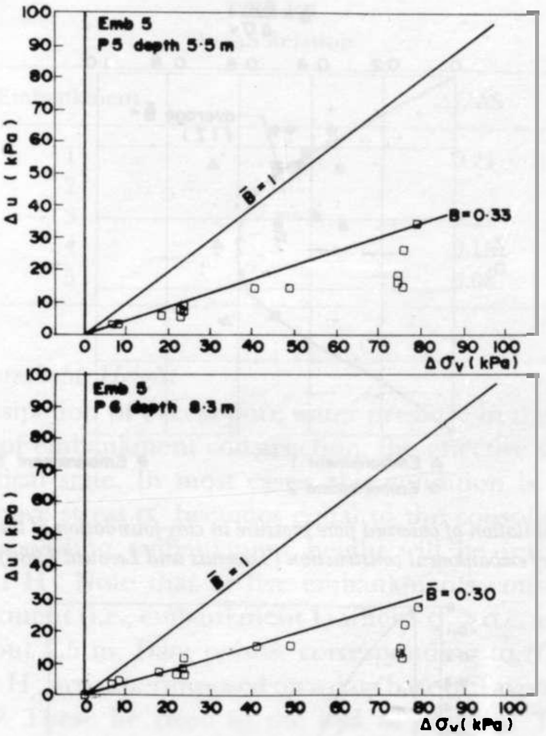


Fig. 6e. Δu - $\Delta\sigma_v$ *relation (embankment 5)*

Tavenas and Leroueil (1980) found the B = f (z) relationship assumes the shape of a consolidation isochrone, despite some scatter with relation:

$$B = \Delta u/\Delta\sigma_v = 0.6 - 2.4\left(\frac{z}{D} - 0.5\right)$$

where z is the depth and D is the layer thickness. The plot is shown in *Fig. 7*. Superimposed on the figure are the data of the present case study. The agreement looks reasonably good. It is remarkable that such a simple relation could be found to describe the complex process of pore pressure generation and partial dissipation during construction; indeed it might be expected that B should depend on rate of construction, soil permeability and compressibility characteristics: boundary conditions, depth of the clay and other details of layering and soil properties.

At the initial stage of the construction, the settlements beneath the embankments are small (*Fig. 8 (a) and (b)*), and so are the lateral displacements. The magnitude of lateral displacement (Δy) is approximately equal to 0.08 - 0.21 centreline settlement increment (ΔS) (Table 1). The above $\Delta y/\Delta S$ relations, except those of embankments 3 and 5, are similar to those reported by Tavenas *et al.* (1979), Jardine and Hight (1987) and Suzuki (1988), who found that $\Delta y = (0.21 \pm 0.03)\ \Delta S$.

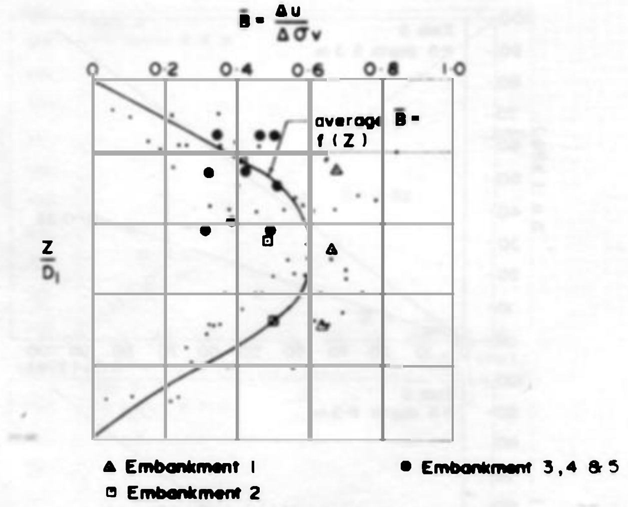


Fig. 7. Compilation of observed pore pressure in clay foundation of the early stage of embankment construction (Tavenas and Leroueil 1980)

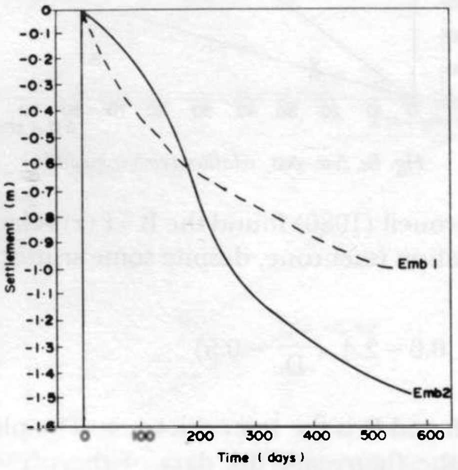


Fig. 8a. Centreline settlement of embankments 1 and 2

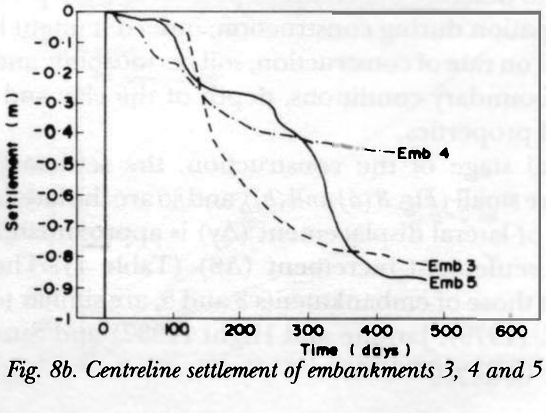


Fig. 8b. Centreline settlement of embankments 3, 4 and 5

TABLE 1
$\Delta y/\Delta S$ Relation

Embankment	$\Delta y/\Delta S$
1	0.21
2	
3	0.11
4	0.16
5	0.08

Embankment Threshold Height

Due to rapid dissipation of excess pore water pressure in the subsoil during the initial stage of embankment construction, the effective stresses increase rapidly to a critical state. In most cases, this condition is achieved when the vertical effective stress σ' becomes equal to the consolidation pressure σ c. The corresponding embankment height will be referred to as the threshold height H_c. Note that of five embankments considered, only in the high embankment (i.e., embankment 1) where $\sigma'_v > \sigma$ c, and its threshold height H_c is about 2.5 m. Data points, corresponding to σ'_v and σ_c at the threshold height H_c, are superimposed on a data base of Tavenas and Leroueil (1980) in *Fig. 9*. These lie close to the line of equality. The clay at this stage becomes normally consolidated.

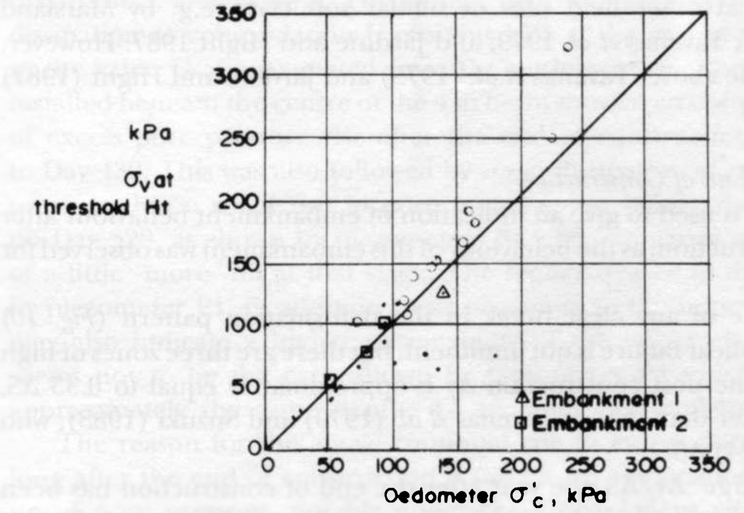


Fig. 9. Threshold efffective vertical stress from pore pressure observation and preconsolidation pressure in embankment foundation (Tavenas and Leroueil 1980)

Behaviour after the Threshold Height (during Construction)

Once part of the foundation has become normally consolidated, the properties of the clay become significantly modified. Their consolidation characteristics are significantly reduced, and further construction occurs under almost undrained conditions. According to the critical state theory (Roscoe and Burland 1968) the effective stress path then follows the critical state curve. The pore pressure increment should then be equal to the embankment load increment. This is shown in the pore pressure - vertical stress plot in *Fig. 6 (b)*. In the case of embankment 2, the pore pressure ratio after the threshold height is approximately equal to $0.8 - 0.9\ \Delta\sigma_v$.

Leroueil *et al.* (1978) found $B = 1.05 \pm 0.15$, similar to the above. A similar observation was also made by Ramalha *et al.* (1983) and by Jardine and Hight (1987). It appears that the occurrence of $B = 1.0$ in the later stages of construction on clay foundation is not due to the development of confined failures as suggested by Hoeg *et al.* (1969), but merely to the passage of the clay to a normally consolidated state.

As for the deformation behaviour during this phase of construction, the clay is subjected to an undrained distortion. The compressibility of the clay is significantly increased, giving rise to large settlement and lateral displacement.

The rate of lateral displacement increase was found to increase with larger (undrained) settlement towards the end of construction. In the case of embankment 2, $\Delta y = 0.3\ \Delta S$ (see also *Fig. 10*). This increase in the rate of lateral displacement with increase in undrained settlement has also been observed at other field sites of similar soft clays, e.g. by Marsland and Powel 1977; Tavenas *et al.* 1979; and Jardine and Hight 1987. However, in contrast to the above, Tavenas *et al.* (1979) and Jardine and Hight (1987) found $\Delta y = \Delta S$.

Behaviour after End of Construction

Embankment 2 is used to give an indication of embankment behaviour after the end of construction, as the behaviour of this embankment was observed for a longer period.

The absence of any clear break in the deformation pattern (*Fig. 10*) indicates that a shear failure is not imminent, but there are three zones of high shear strains. The post construction Δy is approximately equal to $0.33\ \Delta S$, apparently higher than that of Tavenas *et al.* (1979) and Suzuki (1988), who found $\Delta y = (0.24)\ \Delta S$.

However, large $\Delta y/\Delta S$ one year after the end of construction has been reported by Jardine and Hight (1987). They attributed this to the effect of undrained creep.

Fig. 5 shows a pore pressure record of embankment 2. Piezometers P4, P5 and P6 installed beneath the centre of the embankment showed a continual rise in excess pore water pressure from the end of construction at Day 234 to

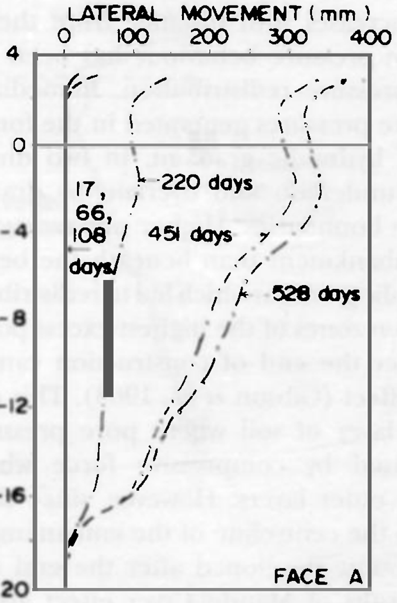


Fig. 10. Lateral deformation of embankment 2

Day 300, followed by commencement of excess pore water pressure dissipation, albeit slowly. The average degree of excess pore water pressure dissipation or consolidation U is about 15% at the end of the record, close to the value U approximated from the settlement. Piezometers P2 and P3 installed beneath the centre of the 4 m berm showed an even longer duration of excess pore pressure rise after the end of construction, from Day 234 to Day 430. This was also followed by some dissipation of excess pore water pressure, but a small rise in pore pressure just before the end of record on Day 528, as shown by piezometers P4 - P6, coincides with the addition of a little more fill at that stage. The higher degree of dissipation shown by piezometer P1, in addition to its proximity to the upper drainage layer, may also indicate a higher permeability of the upper clay layer, but this seems not to be the case, shown by piezometer P4 which was located at approximately the same depth, 4.5 m below the embankment centre.

The reason for the above continual rise in excess pore water pressure long after the end of construction is not clearly understood, but this build-up of pore pressure, notably under the embankment edge (piezometers P2 and P3), coincided with the large post-construction $\Delta y/\Delta S$ described earlier. A continual rise in pore pressure after the end of construction was also observed in 11 out of 31 case histories reviewed by Crooks *et al.* (1984), and in the centrifuge model studies of Davies and Parry (1985). Of particular interest, also, is the time taken for the piezometers to reach their peak values after the end of construction. According to Davies and Parry (1985), this increases with distance from the embankment centre. This anomalous pore pressure behaviour has been attributed by them to the effect of pore pressure redistribution. Immediately after the end of construction, the pore pressures generated in the foundation layer resulted in the formation of hydraulic gradient, in two dimensions for the case where the clay was underlain and overlain by drainage layers, resulting in flow towards these boundaries. Higher pressures generated beneath the centreline of the embankment than beneath the berm (and toe) resulted in a horizontal hydraulic gradient which led to redistribution of pore pressures in the foundation from zones of the highest excess pore pressures. Increases in pore pressure after the end of construction can also be attributed to the 'Mandel-Cryer' effect (Gibson *et al.*, 1963). This results from continuity of a consolidating layer of soil where pore pressure in the interior of the layer rises, caused by compressive force which results from the consolidation of the outer layers. However, since this effect will be most noticeable nearest to the centreline of the embankment where only a small percentage of peak value developed after the end of loading, it must be assumed that the results of Mandel-Cryer effect are, at the most, minor, and may be considered negligible. In addition, there may also be an element of progressive shearing. Embankment loading produces zones of high shear strain, which generate high excess pore water pressures. This may lower the effective stress in the zone sufficiently to permit more shear strain to develop. In turn, this shear strain results in generation of further excess pore water pressure, and strain. Unfortunately, however, there are insufficient piezometric data in the trial embankment (2) under discussion to separate the contribution towards excess pore pressure redistribution or progressive shearing. However, in the author's opinion, owing to the low permeability of the clay, progressive shearing is likely to be more dominant than that of redistribution. Of practical importance, the above indicates that delayed embankment failure can occur under these conditions. However, when noticeable dissipation began at all transducer locations from Day 430 onwards, progressive strengthening of the foundation must have resulted, giving an increased factor of safety against shear induced failure. Any local failure that may have occurred in the foundation close to the embankment shoulder should have been contained by the wide loading berm. *Fig. 11* shows an increase in soil strength with time beneath the centre of embankment 2.

Piezometric Response away from Centreline

No attempt was made by Tavenas and Leroueil (1980) to summarize pore pressure behaviour away from the centreline. Reference to the present study indicates rapidly varying excess pore water pressures under the edge of embankment 1 where potential instability was developing. The piezometric response plotted in *Fig. 12* indicated pore pressure ratio, B 0.5 for fill height

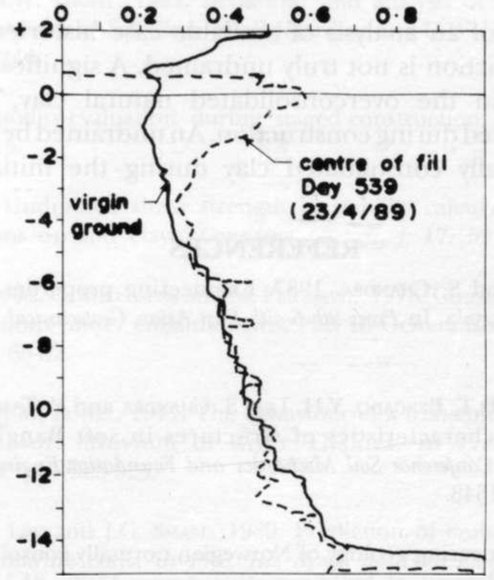


Fig. 11. Results of cone penetration testing beneath fill and in virgin ground of embankment 2

of 0 to 2.5 m (H_c), B 1.0 for fill height of H_c to completion of the berm (H = 4 m), and was followed by a substantial rise in Δu, except at the location of piezometer P1, where pore pressure dissipation apparently exceeded that of generation. Similar observations of rapidly varying excess pore water pressure under the embankment shoulder and toe have also been made by D'Appolonia *et al.* (1971), Davies and Parry (1985) and Jardine and Hight (1987).

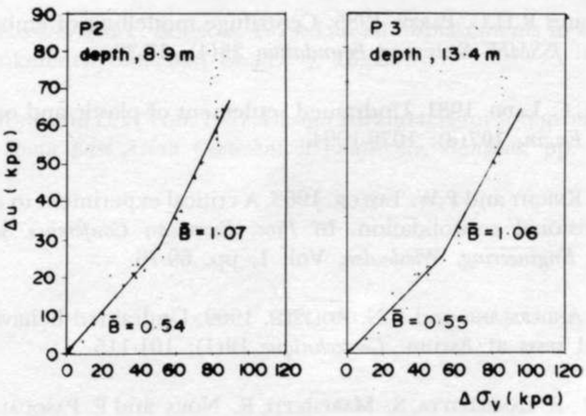


Fig. 12. Edge piezometric response of embankment 2

CONCLUSION

The main finding of an analysis of available case histories is that the clay response to construction is not truly undrained. A significant consolidation develops initially in the overconsolidated natural clay, which becomes normally consolidated during construction. An undrained behaviour develops only in the normally consolidated clay during the initial stages of the construction.

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ISSN: 0128-7680
Pertanika J. Sci. & Technol. 2(2): 237-241 (1994)

COMMUNICATION

Mass Transfer in a Closed-cycle Solid-liquid Extraction Unit

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Received 29 April 1993

ABSTRAK

Pengekstrakan pepejal-cecair merupakan satu proses yang utama dalam industri gula di mana sukros dari bit gula diluluh larutkan dengan menggunakan air panas sebagai pelarut. Dalam kajian simulasi ini, pekali pemindahan jisim pepejal-kepada-bendalir ditentukan dengan mengukur kadar pengesktrakan gula dalam sebuah pengekstrak berkitar tertutup. Pengukuran dilakukan bagi empat kadar aliran: 3.0, 3.5, 4.0 dan 4.5 ml/s pada julat suhu 45 - 65°C pada tekanan atmosfera. Kesan suhu dan halaju pelarut ke atas pekali pemindahan haba adalah positif dan tenaga keaktifan yang dihitung bagi proses pengekstrakan didapati berada dalam julat 4.0 - 5.4 kJ/kmol K.

ABSTRACT

Solid-liquid extraction is a very important process in the sugar industry, in which sucrose from sugar beets is leached by utilizing hot water as a solvent. In this simulation study, solid-to-fluid mass transfer coefficients were determined by measuring extraction rates of sugar in a closed-cycle extractor. Measurements were made for four flowrates: 3.0, 3.5, 4.0 and 4.5 ml/s over a temperature range of 45 - 65°C at atmospheric pressure. The effects of temperature and solvent velocity on mass transfer coefficients were found to be positive, and the calculated activation energies for the extraction process were found to be in the range of 4.0 to 5.4 kJ/kmol K.

INTRODUCTION

Solid-liquid extraction is a very important process in the sugar industry, in which sucrose from sugar beets is leached by utilizing hot water as a solvent (Madsen 1990). There are many types of extractors used in the sugar industry but many use the counter-current arrangement (Chen 1985). To the food process engineer, the major problems associated with the extraction process are the factors affecting the rate of extraction and the establishment of process conditions which ensure the optimum extraction rate (Brennan *et al.* 1990).

The objective of this study was to simulate the leaching process and report on the effect of temperature and solvent flowrate on the solid-to-fluid mass transfer coefficients, which were determined by measuring extraction rates of sugar in a batch closed-cycle extractor.

THEORY

The rate of extraction, dN/dt, of a mass component, N, is described by equation (1):

$$\frac{dN}{dt} = K_L A (C_s - C) \qquad (1)$$

where $K_L A$ represents the overall mass-transfer coefficient across an effective external surface area, A, and C and C_s represent the concentrations of the solute in the solvent at any time, t, and at the saturation condition respectively (Heldman and Singh 1981). If the solid-liquid extraction is carried out in a batch process in which the total volume, V, of solution is kept constant, the following expression is obtained:

$$dN = V\,dC \qquad (2)$$

which leads to the integrated solution in the form:

$$C = C_s \left[1 - \exp\left(-\frac{K_L A}{V} t\right)\right] \qquad (3)$$

Equation (3) implies that the mass-transfer coefficient, the interfacial area between the solid particles and the solvent and the total volume of the solution used will influence the rate at which the solvent approaches the saturation concentration.

MATERIALS AND METHODS

The leaching process was carried out in a closed-cycle extraction unit (Armfield, England, Model UOP4) which is shown diagrammatically in *Fig. 1*. In this study, sugar-impregnated vermiculite of fixed weight was placed in a removable retaining bag inside a small solid-liquid extractor vertical column. Solvent was drawn from a feed tank solvent vessel by a meter pump at a known and constant feed rate and delivered to the extraction column. In this manner the sugar-impregnated sample was washed with a constant volume of hot water. Samples were taken at the outlet stream and the amount of soluble sugar extracted in the system was monitored periodically with a refractometer (Atago, Japan, Model N20) and reported in concentration units of Brix.

Measurements were made at four different solvent flowrates: 3.0, 3.5, 4.0 and 4.5 ml/s over a temperature range of 45-65°C at atmospheric pressure.

RESULTS AND DISCUSSION

The calculated mass transfer coefficients ($K_L A/V$) were found to be in the range of 0.020 – 0.043 min^{-1} and these were correlated with the solvent

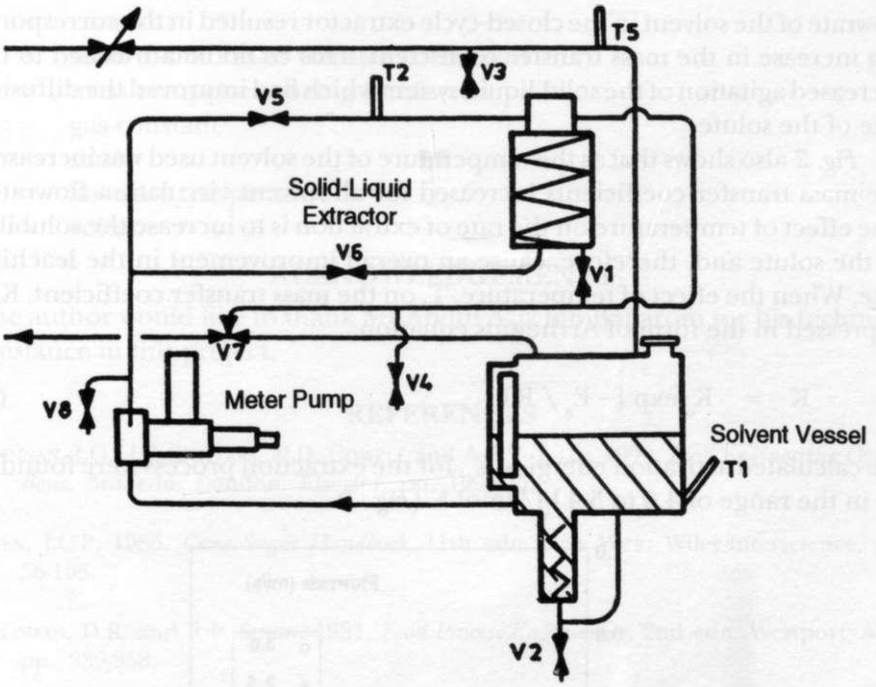

Fig. 1. Schematic diagram of solid-liquid extraction unit where V are valves and T are thermometers

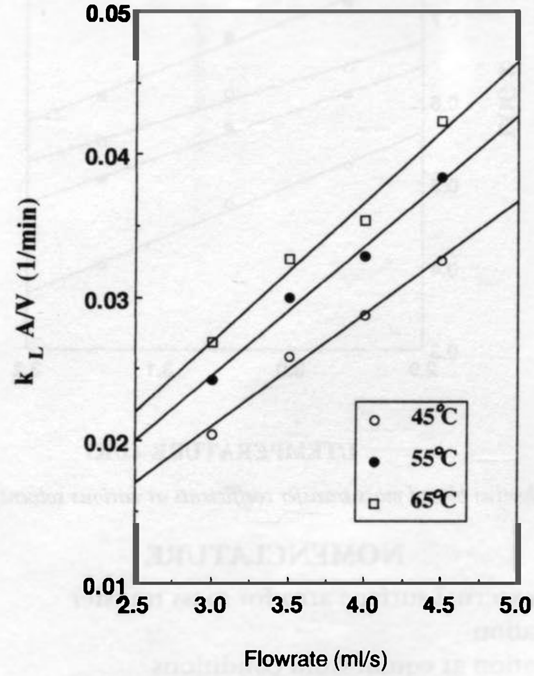

Fig. 2. Mass transfer coefficients with varying solvent flowrates at various temperatures

flowrate of the solvent in the closed-cycle extractor resulted in the corresponding increase in the mass transfer coefficient. This could be attributed to the increased agitation of the solid-liquid system which had improved the diffusion rate of the solute.

Fig. 2 also shows that as the temperature of the solvent used was increased, the mass transfer coefficients increased for all solvent circulation flowrates. The effect of temperature on the rate of extraction is to increase the solubility of the solute and, therefore, cause an overall improvement in the leaching rate. When the effect of temperature, T, on the mass transfer coefficient, K, is expressed in the form of Arrhenius equation:

$$K = K_o \exp\left[-E_a / RT\right] \qquad (4)$$

the calculated activation energies, E_a, for the extraction process were found to be in the range of 4.0 to 5.4 kJ/kmol K (*Fig. 3*).

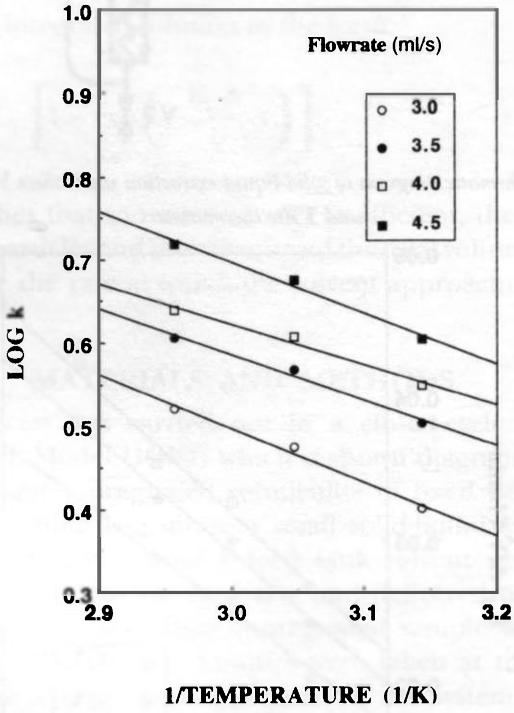

Fig. 3. Arrhenius plot of mass transfer coefficients at various solvent flowrates

NOMENCLATURE

A = effective external surface area for mass transfer
C = concentration
C_s = concentration at equilibrium conditions
E_a = activation energy
K = mass transfer coefficient

K_o = constant
K_L = solid-to-fluid mass transfer coefficient
N = mass component being tranferred
R = gas constant
t = time
T = absolute temperature
V = volume

ACKNOWLEDGEMENTS

The author would like to thank Mr Abdul Aziz bin Baharom for his technical assistance in this project.

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Pertanika Journal of Science and Technology

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Acknowledgement

The Editorial Board acknowledges the assistance of the following reviewers in the preparation of Volume Two of this journal

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Pertanika Journal of Science and Technology

Volume 2 No. 2 July 1994

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