# ABSTRACT

Title of Thesis: Application of Microwave Energy to
Remediation of Soils Contaminated with
Chromium

Chih-Ju, Master of Science, 1989

Thesis directed by: Leonard Dauerman, Associate Professor
of Chemical Engineering, Chemistry and
Environmental Science

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A process based upon microwave treatment has been developed to render soil non-hazardous after that soil had been classified as hazardous due to heavy metal contamination. It has been applied to chromium-contaminated soil. The object of the present regulations is to prevent damage to water supplies as a result of the leaching of heavy metal ions from the soils. This object is expressed in the standard test for leaching, namely, the EPA EP Leachate test. This process can be used to immobilize metal ions sufficiently to meet the aforementioned standard. The present standard is based upon acid leaching, and not upon bioavailability. Thus it is necessary to effect immobilization. Immobilization can be effected before reaching the vitrification state, therefore, the operating cost is much less. In addition, the object of the

remediation in superfund sites is site-specific and can be based upon the elimination of the bioavailability of the metal ions. It is possible using this process to eliminate the bioavailability of the metal ions by effecting vitrification of the soil.

Soil constituents do not absorb microwave radiation strongly at ambient temperatures because their rotational relaxation times are too long even if they are polar; additives decrease the rotational relaxation times. The additives absorb microwave energy strongly and get heated to high temperatures; the heat transferred to the soil constituents decreases their relaxation times and thus they become strong microwave absorbers. The additives chosen for this study were iron and granulated activated charcoal (GAC), respectively. The iron was chosen because scrap iron could be used and that would add little to the cost of the process; the GAC, because spent hazardous waste-contaminated GAC could be used, and in this way two different hazardous waste streams could be destroyed at the same time.

In addition to establishing that the above processes are realizable, studies were undertaken to determine the cost-efffectiveness of the process. These were bench-scale studies so the applicability of the calculations to scale-up is tenuous. However, the reactor designed and the parameters defined can be used in pilot plant studies. Such studies which will conmmence shortly in the future will provide a more realistic assessment of the cost-effectiveness of the process.

The reactor is designed to simulate the exposure of a core of the soil either on the surface or in the bulk to an ascertainable microwave power. That quantity of power can be dertermined either by a power meter or the absorption of the power by water. The latter method was used in this study. The cores were sampled over a range of depths to determine the degree of immobilization of the chromium.

Studies were also undertaken to develop design parameters which could determine the depth of penetration of the incident microwave radiation. These were compared to depths of penetration as calculated by standard methods.

# Application of Microwave Energy to Remediation of Soils Contaminated with Chromium

by

Chih-Ju Jou

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I like to present this thesis to my dear parents, ---- 周彥雄，周殷素碧, sister,--- 周文斐 and brother,--- 周傳超, as the greatest gift in this year, 1989.

Finally, I have to thank all my friends for their supportive and sincere attitude.

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## A. INTRODUCTION

### 1. The Environmental Problem:

The Resource Conservation and Recovery Act ( RCRA ), and the more recent Hazardous and Solid Waste Amendments( HSWA ) have provisions aimed at reducing the use of land disposal for the management of hazardous wastes ( see "The Regulatory Framework", in page 3 of this thesis ). It is well known that the most satisfactory solutions to hazardous waste problems are those which either destroy or detoxify the wastes. However, for the near future, there exist wastes which can not be destroyed or detoxified, but only reduced in volume or contained. These wastes and the residues from their treatment will continue to be managed by land disposal until new technologies for their total destruction emerge. The chromium contaminated in soil is one of the hardest environmental problems. Nowadays, the development of cost-effective technology for the treatment of these hazardous and toxic wastes is becoming more important and necessary.

Concerning the effect of chromium on human health, there is evidence that chromium becomes a toxic substance in the body when it surpasses a certain level. Toxicity is confined almost entirely to the hexavalent chromium compounds. Toxic reactions with trivalent chromium require very high parenteral doses. Chronic exposure to chromate dust results in a high incidence of respiratory diseases, especially lung cancer.(17, 18) In experimental animals, excessive amounts ( 50. ppm ) of orally administered chromate caused growth retardation, liver and kidney damage, respectively.(19, 20)

One example of chromium's toxic affects on health can be seen in the case of Jersey City, New Jersey. In some chromium production plants, manufacturers did not treat the residues of the chromium products properly. This caused a tremendous chromium pollution in Jersey City. The chromium pollution sites of Jersey City have since been designated as superfund sites by the EPA ( Environmental Protection Agency ). Some of the superfund sites in Jersey City have chromium-contaminated soil concentrations over 50,000 ppm.

The results of chromium contamination have serious consequences. Exposure to chromium-contaminated dust will result in lung cancer, and because of chromium's high corrosiveness the ground water supply could become polluted. In addition, chromium contamination has also effected the surrounding infrastructure. It has caused the corrosion of roads and buildings. In order to protect the safety of the ground water and human health, environmental protection workers must work very hard to meet these demanding challenges.

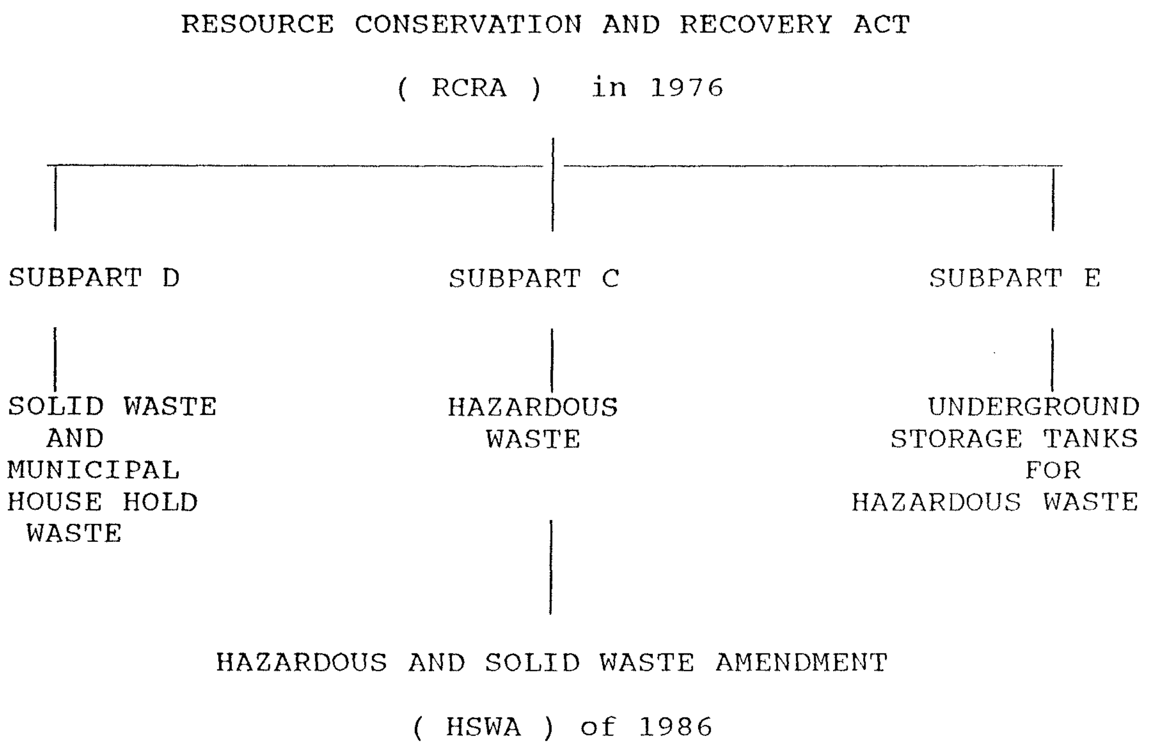
## 2. The Regulatory Framework:

Heavy metal contamination in soil, specifically chromium, is required under the Resource Conservation and Recovery Act which is called RCRA. The RCRA law was passed by the U. S. Congress in 1976 and was signed by the President of the United States. The RCRA includes three subparts which are subpart C, D and E. The subpart C includes hazardous waste. The subpart D includes solid waste and municipal household waste, and the subpart E includes underground storage tanks for hazardous waste. For this particular situation, with regard to heavy metals contaminations in soil such as chromium, the appropriate subpart of the RCRA is the subpart C called hazardous waste program.

Under the RCRA, four heavy metals have been regulated. They are the following:

(1) Cr ( Chromium )
(2) Pb ( Lead )
(3) As ( Arsenic )
(4) Hg ( Mercury )

RCRA was amended in 1986. Those amendments are called the Hazardous and Solid Waste Amendments of 1986, more commonly referred to by the acronym HSWA.



The HSWA requires the specific regulation of the treatment of storage and the disposal of hazardous wastes. Four specific standards developed by the EPA are as followings:

(1) Generator's standards,

(2) Storage standards,

(3) Treatment standards,

(4) Disposal standards.

For example, the chromium action level in the standard leachate test adopted by the EPA is 5.0 mg/liter. The aforementioned tests is the EP TOXICITY TEST PROCEDURES which is in the 40 CRF 261.1. Under the HSWA program, chromium in a substrate can not be put into a landfill, if that substrate contains more than 2 % of water ( Federal Register 263.5, in 1987 ).

## 3. Remediation Technologies:

Essentially, the hazard associated with a toxic heavy metal in soil is related to its bioavailability. The only way to render a toxic heavy metal non-hazardous is to eliminate its bioavailablibity. This can be affected by encapsulating the heavy metal into a matrix which in itself is not bioavailable. The following remediation technologies are being discussed and their appropriateness for immobilizing chromium. Illinois Institute of Technology ( IIT ) developed the RF (Radio Frequency) technology; Pacific Northwest Laboratory ( BATTELLE ) developed electric-current vitrification technology. Both of them are available for use now. The technology of Stabilization/Solidification ( S/S ) and the application of microwave energy treatment ( MW ) of NJIT are in development. These four technologies are described below.

IIT developed the techniques of radio frequency ( RF ) in-situ heating. These techniques can be used for the treatment of soils containing hazardous chlorinated hydrocarbons. RF heating is used to heat the soil to the treatment temperature to facilitate decontamination at an average heating rate of 0.8 to 1.0 $^{o}$C. The feasibility of soil decontamination by thermal recovery of low boiling contaminants and chemical treatment of high boiling materials such as PCBs with dehalogenation agents, has been established. In-situ RF heating is accomplished by inserting tubular electrodes into portholes or by laying horizontal electrodes over the surface of the soil and by energizing them with an RF power source. The electrode pattern is selected based on the depth of penetration of the contaminant and the required temperature. The operating frequency is selected on the basis of the electromagnetic characteristics of the soil. Vapor and gas containment and collection systems are used to enclose the treated module.(13)

The IIT RF technology reaches a very low maximum temperature. It is only 400 $^{o}$C. At this temperature it would not be possible to immobilize chromium.

BATTELLE developed the techniques of consolidation of soil by applying the voltage difference between electrodes. The process uses an electric current that is passed between electrodes placed in the ground. It converts soil and contained materials to a stable glass material. This is named vitrification of soil. Heat from the electric current melts the soil and rocks and decomposes organic materials. During the process, metallic and other inorganic materials are dissolved into or are unencapsulated in the vitrified mass. Gasses evolve from the melt or go into solution. Convective currents within the melt uniformly mix materials that are present in the soil. When the electric current ceases, the molten volume cools and solidifies. In situ vitrification can be used in most known soils, including those saturated with water ( not free flowing ) and those that contain a variety of mixed, buried materials.(12)

S/S techniques are used to treat the contaminated soil with the conception of stabilization and solidification of contamination in soil. They are applicable to the treatment of selected banned waste prior to landfilling, and also applicable to the treatment of residues from other treatment technologies.(15) To this day, the observed results are the followings:(16)

1. The water-to-total-solids ratio appears to be a better measure of the amount of water needed to be solidified a given mix than the water-to-binder ratio that is commonly used. This was clearly the case for the " Synthetic Analytical Reference Matrix ( SARM ) with these binder. This needs to be confirmed on other systems.

2. Solidifying the SARM resulted in significant reduction in the amount of metal salt contaminants released, as measured by the Toxic Contaminants Leaching Procedure ( TCLP ).

3. Solidification did not appear to result in a similar reduction in the amount of organic emissions from the SARM.

4. No correlation between Unconfined Compressibility (UCS) testing and the results of the leaching tests was observed.

5. These S/S techniques have virtually no effect on the chromium ions.

NJIT has been developing a method which applies the microwave energy to immobilize the chromium. This treatment method, used to immobilize metal ions (chromium), is sufficient to meet the aforementioned standard by EPA.

It has been found by this research group that soil can be converted into the vitrified and non-vitrified state in a microwave oven with no additives or with additives such as granulated activated charcoal(GAC) or metallic iron. In the case of iron it has been observed that the iron melts which means that at least, the melting temperature of iron has been reached, namely, 1500$^{\circ}$C. These observations lead to immediate questions as to the properties that a substance must have to make soil vitrification possible. Iron and GAC heat rapidly when exposed to microwave irradiation, both arc, and both are reducing agents. This thesis deals in obtaining the effectiveness of the process and to guide future studies.

TABLE 1 shows the comparison of the three research groups --- IIT, NJIT, and BATTELLE.

# TABLE 1

## METHODS to TREAT the CONTAMINATED SOIL :

## IIT, NJIT, and BATTELLE

| research group / properties | IIT | NJIT | BATTELLE |
|---|---|---|---|
| Energy source | radio wave | microwave | voltage difference |
| Highest Temperature | 400°C | 1500°C | 2000°C (3600°F) |
| Heating speed | 0.8 to 1.0 °C/hr | within several min. reach about 900°C | function of depth and electrode spacing |
| Treatment concept for inorangics | NOT vitrified | vitrified | vitrified |
| Treatment method for orangic compounds | decomposed directly and steam distillation | steam distillation | decomposed directly |
| Additives | no | G.A.C. and iron wires but not necessary | graphite ( as path of current) |
| Types of materials treated | orangics of low molecular weight | orangics and inorganics | orangics and inorangics |

## B. MICROWAVE THEORY

Microwave (MW) energy is composed of an electric field and a magnetic field. It is a form of electromagnetic radiation, with the frequencies ranging from 100 MHz ( 3 meters wavelength ) and 300 GHz ( 1 millimeter wavelength ). The electric field interacts with polar materials, molecules with dipole moments, and the magnetic field interacts with magnetic materials or charged particles in motion.

Basically, there are three classes of materials in a MW processing system : (1) conductors (2) insulators (3) dielectrics. Most good conductors are metallic such as aluminum, brass, copper etc. These conductors reflect microwaves except the ones with sharp edges. The reflective property of conductors is used to advantage in containing and directing microwave. For example, a wave guide is a closed high-conductivity metallic tube which guides the microwaves to a specific location where they are needed to perform the work. The wave guides are commonly made out of aluminum or brass and are usually with rectangular cross section. Secondly, insulators, they reflect and transmit microwaves and usually absorb only a very small amount of MW energy ( partial reflection and transmission, negligible absorption ). Teflon, polypropylene etc, play a useful insulator part in a MW system.

Thirdly, dielectrics, they have the properties in between insulators and conductors. In the area of MW power, dielectrics absorb MW energy in varying degrees and the materials to be treated have dielectric properties.

The degree of reflection and penetration for a special material depends on its dielectric properties. Here, penetration means " Penetration Depth " ( PD ) which is defined by the depth at which 50% of the MW energy is absorbed. The dielectric properties are generally described by four basic parameters which describe the relationship of microwave properties for a particular material at a particular frequency. These are dielectric constant ( e ), loss tangent (tan d ), real part of dielectric constant ( e' ) and imaginary part of dielectric constant ( e" ) which is also called loss factor. The relationship of these parameters are defined as

$$e = e' - j e'' \qquad (1)$$

$$\tan d = e'' / e \qquad (2)$$

where, -j indicates a 90o phase shift between the real and imaginary part of the dielectric constant.

What properties of materials determines the absorption of microwave energy? It is known that the dielectric constant of a materials plays an important role. But what is a dielectric constant? It is a property which is not, as the name implies, a constant. To the contrary, a material's dielectric property depends on many parameters which can be described as the followings:

(1) Moisture content: The amount of moisture in a substance greatly affects the dielectric constant of the material. The reason is that water has a very high dielectric constant ( approximately 80 ), whereas the base materials have a dielectric constant of much lower value ( usually around 2 at room temperature ). Generally, the higher the moisture content the higher the dielectric constant. Furthermore, the dielectric loss usually increases with increasing moisture content.

(2) Temperature: The dielectric constants are temperature dependent which means they are functions of temperature. Temperature dependence of dielectric constants are quite complex in nature. Generally, the dielectric loss is decreased with increasing temperature, i.e, the dielectric constant is increased while the temperature is increased and the loss tangent is also increased. Both temperature and moisture content are the important variables in a microwave heating or drying ( dehydration ) process. At a high temperature ( close or above 100 $^{o}$C ) or at very low moisture content, dielectric constant and loss are a strong function of temperature and the relaxation time is shorter than that at a low temperature. Relaxation time is a delayed response to a changing stimulus.

(3) Geometric factors: The surface area and the shape of the material is important to affect the absorption of microwave energy. Usually, the material with sharp edges is more

microwave energy absorbable and the surface area exposed to the energy field is almost proportional to the absorption of microwave energy.

(4) Density: The density of a material can affect the value of the complex dielectric constant. For example, the dielectric constant of air is 1.0 at room temperature and air is for all practical purposes considered mainly transparent to microwave energy. All other non-gaseous materials have dielectric constants larger than one. Therefore, air inclusions will always reduce the dielectric constant of a materials below the value which the material has no or little air. As the density of a material increases so does its dielectric constant.

There are several other parameters which will affect the absorption of microwave e.g., frequency of microwaves, conductivity of a material, specific heat of the material and physical and chemical structure of the material, etc.

Another important aspect related to this thesis is the penetration depth. It is a measure of the effectiveness of microwave energy absorption, and strongly affects the size of the operation load and the design of the reactor. Moreover, the dielectric constant and the dielectric loss determine the depth of effective energy penetration into a material. The penetration depth ( PD ) is defined as

$$PD = \frac{\lambda_o (e')^{1/2}}{2.88 \pi (e'')} \qquad (3)$$

where, $\lambda_o$ is the free space wavelength in cm defined by c/f, c being the velocity of light in cm/sec and f being the frequency. Since the wavelength is a function of the medium, it is the property of the material while entering the material. This represents that PD is also a function of wavelength.

An approximate formula for calculating absorbed power of microwave energy is given as

$$\text{Power}_{(abs)} = (55.61*10^{-14}) * f * E^2 * e'' \qquad (4)$$

in watts/cm$^3$. where, f, is the frequency after entering the material in cycles/sec, E, is the electric field strength in volts/cm ( for example, a rate of temperature rise of 1.0 $^oC$/sec has to correspond to a electric field ( E ) of 15.8 volts/cm (RMS) or 22.4 volts/cm peak within the water ) and e" is the dielectric loss, which is a function of dielectric constant ( e ) and tangent loss ( tan d ).

For instance, using the equation (4), the absorbed power ( $\text{Power}_{(abs)}$ ) of distilled water at 20 $^oC$ placed in a microwave field with a 2450 MHz frequency can be calculated.

In water and at 20 $^oC$,

$f = 2450$ MHz $* ( 3/2) = 3675 * 10^6$ cycles/sec

$E = 22.4$ volts/cm

( at 1 $^o$ C/sec temperature rise )

$e = 78.$

$\tan d = 0.16$

Since,

$$e'' = e / \tan d \qquad (2)'$$

Therefore,

$$e'' = 78. * 0.16 = 12.48$$

Using the equation (4), the $\text{Power}_{(abs)}$ is calculated by inserting the data of f, E and e",

$$\text{Power}_{(abs)} = 55.61*10^{-14}*3675*10^{6}*22.4^{2}*12.48$$
$$= 12.80 \qquad \text{watts/cm}^{3}$$

The calculation of power absorption of distilled water is a basic application of the fundamental formula. Furthermore, it can be applied to calculate the power absorption of the complex material like soil.

Since, the dielectric constant (e), dielectric loss (e") and tangent loss (tan d) are functions of temperature in this case, the calculation can be done by measuring the values of these parameters from experiments or making a theoretically reasonable assumption of them at the condition. This work is not included in the studies of this thesis. But it is possible to approximate the absorption of microwave energy from the dielectric properties and the above equations.

## TEABLE 2

### A Partial List of Dielectric Properties of Some Materials at 2450 MHz Microwave Radiation (at room temperature, 20 $^{o}$C)

| Material | e | tan d |
|---|---|---|
| Distilled water | 78 | .16 |
| Clay, 20 % $H_2O$ | 11.3 - 20 | 0.25 - 0.5 |
| $SiO_2$ | 3.78 | .0005-.0010 |
| NaCl | 5.90 - 5.98 | < 0.0003 |
| Se (crystalline) | 10.4 - 11.0 | 0.1 - 0.25 |
| MgO | 3.62 | < 0.0003 |
| $H_2O$ (ice) | 3.17 - 3.3 | .0007-.0010 |
| Ceramic (Aluminium) | 8 - 11 | .0001 - .001 |
| Most Plastics | 2 - 4.5 | .001 - .02 |
| Smoe Glasses (Pyrex) | ~ 4.0 | .001 - .005 |
| Papers | 2 - 3 | .05 - .1 |
| Woods | 1.2 - 5. | .01 - .1 |

## C. THE OBJECTIVES

The objective of the experiment is to study the immobilization of chromium in soil on the bench-scale. The reason for the investigation stems from environmental concerns over contaminated soil by heavy metal ions - Chromium ( Cr ) has been responsible for polluting groundwater and also causes undesirable biological effects such as cancer and other illness.

Through microwave energy, it is expected that the ions of chromium will become immobilized causing a bonding with the soil. If this occurs, leaching will be prevented.

Another objective of this experiment is to try to develop parameters to be used for an analysis of the feasibility of the process in a pilot plant scale. By investigating the process on a bench-scale, it is possible to characterize the factors affecting the microwave energy absorption, and the design of the pilot plant can be made based on the parameters. Estimations of the parameters of the pilot plant scale can be determined through the study of bench-scale experiments.

## D. METHODS

In order to achieve the objectives, it is essential to determine the absorption of microwave energy as related to chromium-contaminated soils. The following approaches will be examined. The first step involves the measurement of the incident power absorbed by water; the second step, the studies of the immobilization of the metal on a bench-scale.

The experimental set-up is designed so that the absorption power of microwave energy and the exposure time of microwave energy can be calculated. In order to accomplish this, a test tube is placed in a large beaker and is surrounded by sand. The beaker is completely covered with aluminum foil, leaving only the top of the test tube exposed. Since the aluminum foil reflects the microwave radiation, the only way the microwave radiation enters the test tube is through the top. Furthermore, the heat build up of the material within the test tube is largely confined within the material as the sand acts as an insulator.

The initial approach is to determine how much microwave power enters the test tube and how much is absorbed by the reactor. Also, the penetration depth of the radiation. The assumption is made that water absorbs maximally the microwave energy. By measuring the time it takes water to boil, the absorption power of microwave radiation can be calculated as defined by equation (3) and (4).

After measurement of the absorbed power, the extent of the soil decontamination can be determined.

The test for leachate toxicity is based upon the standard for decontamination of the toxic heavy metal in the soil adopted by the EPA ( the Environmental Protection Agency ) to implement the federal Resource Conservation and Recovery Act (RCRA). The depth of decontamination represents the depth of the soil sample that meets the EP leachate test in both the vitrified and non-vitrified parts of the soil. EP TOXICITY TEST PROCEDURES are used to determine the leachibility of contaminated soil before and after microwave treatment.

The second approach is the following:

Chromium-contaminated soil will be analyzed with no additives by EP toxicity test procedures. The other approach involves studying the effects of the additives of non-contaminated GAC and iron wires ( scrap iron ) to chromium-contaminated soil and will be analyzed by EP toxicity test procedures.

The detailed experimental procedures for the distilled water absorption studies by microwave radiation and the chromium-contaminated soil by EP toxicity test procedures are described in the section one of chapter E and F respectively.

## E. WATER STUDIES

It is important to determine the energy absorbed by the materials in a MW oven. Although the absorption of the MW energy is complex, a series of simple experimental procedures are designed to determine the parameters which affect power absorption and penetration depth ( PD ). The PD is defined as the depth at which 50 % of the MW energy is absorbed. The exposed surface area (S) of reactor, the loading (water) depth of the reactor, and the volume ( V ) of the reactor were designed to be studied and were set up for experiments. The reactor is defined as the test tube (or the beaker) which contains the load. Water is used as the load since it absorbs MW energy very strongly. The data obtained in a MW oven operating with an energy output of 550 Watts and at a frequency of 2450 MHz. FIGURE 15 shows the diagram of the system and reactor. The reactor is covered with aluminum foil on the side and bottom therefore the MW is allowed to enter the reactor only from the exposed surface area which includes the reactor ( test tube plus water ) and the sand bed which acts as an insulator to microwave energy.

### (1). Exposed surface area factor (S)

Five different sizes of reactors which are covered with aluminum foil on the outer surface were used in the experiments. Each group was run with changing length of the Al-covered test tube and the volume of water. TABLE 3 shows the results of these five groups of experiments with Length (H) in cm, Volume (V) in ml, Time (t) in sec and (V/t) in ml/sec. FIGURE 3 gives the (V/t) vis (H) change of these five groups.

### (2). Loading depth factor (H)

This factor is concerned with penetration of energy. Here, three different depth groups are chosen to determine the depth factor. TABLE 4 shows the data of these three groups of experiments with surface area (S) in $cm^2$, Volume (V) in ml, Time (t) in sec and (V/t) in ml/sec and FIGURE 4 gives the (V/t) vis (S) change of the three groups.

### (3). Reactor volume factor (V)

Here, four groups of experiments are designed to determine the volume factor. Each group is run with constant volumes of 30 ml, 60 ml, 100 ml, and 200 ml, respectively, but with different lengths of the Al-covered test tube and surface areas. TABLE 5 shows the data from these four groups of experiments with Depth (H) in cm, Surface area (S) in $cm^2$, Time (t) in sec and (V/t) in ml/sec, and FIGURE 5 gives the (V/t) vs (S) change of these four groups.

## 2. Results and Discussion:

TABLE 3 and FIGURE 3 show that the volume increases with increasing efficiency and the loading depth increases with increasing efficiency when the depth is smaller than 8.5 cm. When the depth is greater than 8.5 cm, the efficiency decreases with increasing depth.

TABLE 4 and FIGURE 4 show that the efficiency increases with increasing exposed surface area and increases with greater volume.

TABLE 5 and FIGURE 5 show that the efficiency increases with greater depth and increasing with increasing of exposed surface area. Since the loading depth used in the experiments are all smaller than 8.5 cm ( maximumally 6.0 cm ), the results are the same as mentioned above.

Equation (3) is used to calculate penetration depth (PD) and equation (4) is used to find the power absorbed by water ($\text{Power}_{(abs)}$) from room temperature ($25^{o}C$) to boiling point ($100^{o}C$).

Because the dielectric constant ( e ) changes from 81.30 ( at 25 $^{o}C$ ) to 57.90 ( at 100 $^{o}C$ ). ( Ref. 7, page E-57 ) and the data related to the tangent loss is limited. Several assumptions were made for the calculation.

(1) It was assumed that e = 69.10. This is an average value of the dielectric constant from 25 to 100 $^{o}$C.

(2) It was assumed that tan d = 0.16 for a temperature range of 25 to 100 $^{o}$C.

For example, the last data of TABLE 3 ( S = 18.49 cm$^{2}$, V = 560 ml, t = 719 sec, and V/t = .78 ) is chosen to be calculated. From equation (3), the PD is equal to 2.45 cm, and from equation (4), the Power$_{(abs)}$ is equal to 242.96 watts at E = 4.0 volts/cm. All other results of the experiments can be calculated by using equation (3) and (4).

Additionally, the variable (V/t) can be used to represent the absorbed power. It can be used to check the results of power absorption from equation (4). "V" is the volume of water and "t" is the time that it takes for the water to reach the boiling point (100 $^{o}$C) from room temperature (25 $^{o}$C). The following thermodynamic statements and mathematical operations specify the use of (V/t):

$$H2 - H1 = Cp * m * (T2 - T1) \qquad (5)$$

where

H2 and H1 : enthalpy in state 2 and 1
T2 and T1 : temperature in state 2 and 1
Cp : heat capacity of water
m : Mass of water in the reactor
V : volume of water in the reactor

$q$ : density of water

since

$$m = V * q$$

therefore

$$H2 - H1 = Cp * V * q * (T2 - T1) \qquad (6)$$

For water in liquid state, density ( q ) and heat capacity ( Cp ) are constants; plus the temperature change (T2 - T1) is almost equal to 75 $^{o}C$.

$$(T2 - T1) = (100 - 25) = 75\ ^{o}C$$

let

$$K = Cp * q * (T2 - T1) \qquad (7)$$

then

$$H2 - H1 = K * V \qquad (8)$$

The power ( P ) is calculated by,

$$P = (H2 - H1) / t \qquad (9)$$

Equation (7) shows that (V / t) is proportional to the absorbed power ( P ) and the reason why (V / t) can represent the characteristic of adsorbed MW energy. Actually, K is a function of temperature, but it can be assumed that it is a constant for water at liquid state and at one atm..

( Here,K= 75 cal/ml for water, at liquid phase and 1 atm..)

The example is chosen the same as the above which V/t is equal to 0.78. From equation (10), the power ( P ) is equal to 245.45 watts which is very close to the value of $\text{Power}_{(abs)}$ ( 242.96 watts )

## TABLE 3

Heating rate of water at fixed exposed surface area (S), but at variable height (H) and volume (V)

1). S = 0.46 $cm^2$

| H (cm) | V (ml) | t (sec) | V/t (ml/sec) |
|---|---|---|---|
| 2.0 | 4.0 | 73 | 0.05 |
| 4.0 | 7.5 | 80 | 0.09 |
| 6.0 | 12.0 | 93 | 0.13 |
| 8.0 | 16.0 | 138 | 0.12 |
| 10.0 | 20.0 | 260 | 0.08 |
| 12.0 | 24.1 | 392 | 0.08 |
| 14.0 | 28.0 | 1604 | 0.02 |

2). S = 7.84 $cm^2$

| H (cm) | V (ml) | t (sec) | V/t (ml/sec) |
|---|---|---|---|
| 3.0 | 62 | 321 | 0.19 |
| 5.0 | 104 | 350 | 0.30 |
| 6.5 | 150 | 380 | 0.40 |

3). S= 10.89 $cm^2$

| H (cm) | V (ml) | t (sec) | V/t (ml/sec) |
|---|---|---|---|
| 3.0 | 82 | 358 | 0.23 |
| 5.0 | 142 | 420 | 0.34 |
| 6.5 | 175 | 440 | 0.40 |
| 7.5 | 250 | 552 | 0.45 |
| 8.5 | 300 | 652 | 0.46 |

4). S= 14.44 $cm^2$

| H (cm) | V (ml) | t (sec) | V/t (ml/sec) |
|---|---|---|---|
| 3.0 | 105 | 266 | 0.39 |
| 5.0 | 188 | 375 | 0.50 |
| 6.5 | 250 | 400 | 0.62 |
| 7.5 | 285 | 482 | 0.65 |
| 10.0 | 400 | 613 | 0.62 |

5). S= 18.49 $cm^2$

| H (cm) | V (ml) | t (sec) | V/t (ml/sec) |
|---|---|---|---|
| 3.0 | 214 | 365 | 0.58 |
| 5.0 | 258 | 422 | 0.61 |
| 6.5 | 350 | 483 | 0.72 |
| 7.5 | 380 | 500 | 0.76 |
| 10.0 | 560 | 719 | 0.78 |

where

H : the height from the bottom to the water surface.

S : the top surface area.

V : the volume of water.

t : the time takes to B.P. of water.

## TABLE 4

Heating rate of water at fixed height (H), but at variable exposed surface area (S) and volume (V)

1). H = 5.0 cm

| S ($cm^2$) | V (ml) | t (sec) | V/t (ml/sec) |
|---|---|---|---|
| 2.56 | 29.0 | 180 | 0.16 |
| 4.00 | 54.0 | 288 | 0.18 |
| 5.30 | 76.0 | 315 | 0.24 |
| 7.84 | 108.0 | 350 | 0.31 |
| 10.89 | 142.0 | 420 | 0.33 |
| 14.44 | 188.0 | 375 | 0.50 |
| 18.49 | 258.0 | 422 | 0.61 |

2). H = 6.5 cm

| S ($cm^2$) | V (ml) | t (sec) | V/t (ml/sec) |
|---|---|---|---|
| 7.84 | 150.0 | 380 | 0.40 |
| 10.89 | 175.0 | 440 | 0.46 |
| 14.44 | 250.0 | 429 | 0.58 |
| 18.49 | 305.0 | 483 | 0.63 |

3). H = 7.5 cm

| S ($cm^2$) | V (ml) | t (sec) | V/t (ml/sec) |
|---|---|---|---|
| 10.89 | 250.0 | 552 | 0.45 |
| 14.44 | 275.0 | 572 | 0.48 |
| 18.49 | 500.0 | 683 | 0.76 |

## TABLE 5

Heating rate of water at fixed volume (V), but at variable height (H) and exposed surface area (S)

1). V = 30.0 ml

| H (cm) | S ($cm^2$) | t (sec) | V/t (ml/sec) |
|---|---|---|---|
| 5.0 | 2.56 | 196 | 0.15 |
| 3.4 | 4.00 | 186 | 0.16 |
| 2.2 | 5.30 | 200 | 0.15 |
| 1.6 | 7.84 | 145 | 0.21 |
| 1.1 | 10.89 | 150 | 0.20 |
| 0.9 | 14.44 | 103 | 0.23 |
| 0.7 | 18.49 | 146 | 0.21 |

2). V = 60.0 ml

| H (cm) | S ($cm^2$) | t (sec) | V/t (ml/sec) |
|---|---|---|---|
| 3.0 | 5.30 | 295 | 0.20 |
| 2.5 | 7.84 | 264 | 0.23 |
| 1.7 | 10.89 | 190 | 0.32 |
| 1. | 14.44 | 156 | 0.38 |
| 1. | 18.49 | 130 | 0.46 |

3). V = 100 ml

| H (cm) | S ($cm^2$) | t (sec) | V/t (ml/sec) |
|---|---|---|---|
| 3.5 | 7.84 | 350 | 0.29 |
| 2.7 | 10.89 | 331 | 0.30 |
| 2.1 | 14.44 | 260 | 0.38 |
| 1.5 | 18.89 | 217 | 0.46 |

4). V = 200 ml

| H (cm) | S ($cm^2$) | t (sec) | V/t (ml/sec) |
|---|---|---|---|
| 6.0 | 10.89 | 751 | 0.27 |
| 5.5 | 14.44 | 501 | 0.40 |
| 4.5 | 18.49 | 460 | 0.43 |

## 3. Conclusion

The smallest and largest volume of those experiments above are 4.0 ml and 560 ml, respectively. There are the results of bench-scale only, but not the results for large scale or pilot plant. However, they will help us to understand the tendency of a larger scale.

The maximum absorption of microwave energy occurs at the following conditions:

(a). Large exposed surface area

(b). Large volume of load ( water )

(c). The water height not greater than 8.5 cm

Condition (a) and (b) imply that a large scale has a better efficiency than a small one. This is good for the build-up of a pilot plant and a real scale-up plant, because they have a high efficiency and low cost. Condition (c) shows that, for water, the design of a load height is not greater than three times of PD ( 2.45 cm ) in order to have a good absorption efficiency. Actually, after three PDs, only 12.5 % of the power input is absorbed, so the efficiency must be low.

## F. CHROMIUM-CONTAMINATED SOIL STUDIES

### 1. Experimental procedures:

#### (1). Preparation of contaminated soil

Procedures:

1. Preparation of 0.1 M $K_2CrO_4$ solution by using distilled water as solvent.
   ( molecular weight of $K_2CrO_4$ = 194.19 g/mole )
2. Weigh 140.0 gm of soil.
3. The volume of $K_2CrO_4$ solution taken depends on the degree of contamination. If the soil is to be contaminated with 260 ppm of chromium, 7.0 ml of 0.1 M $K_2CrO_4$ are diluted to 21.0 ml.
4. Pour $K_2CrO_4$ solution 21.0 ml over 140.0 gm soil and stir until the soil is wet.
5. Place the wet contaminated soil into the microwave oven and heat it to dryness, assuming that only water evaporates.
6. Transfer the dry soil into a beaker, then put the beaker in sand bed which is covered with aluminum foil on the outer surface.

### (2). Specific characteristics of soil

Following is a list with the specific characteristics of the soil which is used in the experiments.

Geologic formation : Brunswick formation
Textural description : Situ and Clay mixture
Place : VETERAN ADMINISTRATION
HOSPITAL, LYONS, NJ.
(Construction site)

The soil and the information of the soil are supplied by Professor John Schuring of the Department of Civil and Environmental Engineering of New Jersey Institute of Technology, Newark, New Jersey.

## 2. EP Leachate test procedures:

The test procedure is a measurement of how much chromium(Cr) will leach from the soil formation. It is named EP TOXICITY TEST PROCEDURES which can be found in 40 CRF 261.1, APPENDIX - II. The EP TOXICITY TEST PROCEDURES is a combination of extraction and separation procedures and it is one of the standard methods of the E.P.A. to test solid wastes. After extraction, it was sent for an Atomic Absorption ( VARIANT TECHTRON MODEL 1200 ) analysis to determine the leachate concentration of chromium from the samples.

### EP TOXICITY TEST PROCEDURES:

Equipment:

1. NBS stainless steel sieve (Cat. # : 75-9501-06)
   opening is 9.5 mm
2. 500 ml Beaker (glass)
3. Magnetic stirring hot plate
4. Teflon coated stirrer
5. Filter paper
6. Funnel
7. 0.5 N Acetic Acid

( 28.7 ml of Acetic acid diluted to 1.0 liter by distilled water. )

8. Ph meter

9. Centrifuge

Procedure:

Take 50.0 gm of the sample and grind it in a grinder to pass through the above size (8") sieve. Weigh again the sieved material and note the weight. Transfer the powdered and sieved material into a 500 ml beaker. Add 16 times its weight of distilled water. (For example, if the weight of the material is 15 gm then (15 * 6 = 240)gm of distilled water of 240 ml of distilled water is needed). Put a teflon coated magnetic stirrer and stir for 15 minutes. The stirring rate is to be such that all the solids should remain in suspension. Measure the Ph value by a Ph meter.

If the Ph value of the slurry is above 5.00: adjust the Ph value to 5.0 + 0.02 by adding 0.5 N acetic acid.

If the Ph value is below 5.00 no addition of acetic acid is needed.

The stirring procedure should be continued for 24 hours and the temperature should be reported between the temperature 20 and 40$^{o}$C.

During the extraction procedure the Ph value of the slurry should be constant and acetic acid should be added if the Ph value rises above 5.00; but in no case more than 4 ml of acid per gm of the solid should be added.

After the 24 hours period, deionized water is to be added to the beaker determined by :

$V = 20(W) - 16(W) - A$

V = volume of water to be added.

W = weight in gm of the solid taken.

A = volume of acetic acid added.

The material in the extractor shall be separated into its component liquid and solid phases as described under " Separation Procedure ".

(1) Following manufacturer's directions, the filter unit shall be assembled with a filter bed consisting a 0.45 micrometer filter membrane. A refilter bed consisting of the following refilters in increasing pore size (0.65 micrometer membrane, fine glass fiber refilter, and coarse glass fiber refilter) can be used.

(2) The waste shall be poured into the filtration units.

(3) The reservoir shall be slowly pressurized until liquid begins to flow from the filtrate outlet at which point the pressure in the filter shall be immediately lowered to 10 - 15 psi. Filtration shall be continued until liquid flow ceases.

(4) The pressure shall be increased step wise in 10 psi increments to 75 psi and filtration continued until flow ceases or the pressurizing gas begins to exit from the filtrate outlet.

(5) The filter unit shall be depressurized, the solid material removed and weighed and then transferred to the extraction apparatus, or, in the case of final filtration prior to analysis, discarded. Do not allow the material retained on the filter pad to dry prior to weighing.

(6) The liquid phase shall be stored at $4^{o}C$ for subsequent use.

After the separation procedure, the slurry is added to distilled water and filtered with a funnel. The filtrate volume is measured and analyzed for the desired components.

The Atomic Absorption operating procedures:

1. Adjust the operating current: 10 mA
2. Adjust the most sensitive line (wavelength): 425.44 nm
3. Adjust the spectral band width (SBW): 0.5 nm
4. Adjust the flame color to the blue:
    (a) the air flow rate is 10.0 SCFH
    (b) the fuel flow rate is 0.9 LPM
5. Use distilled water as a blank test.
6. Run the standard solutions to be a calibration curve.
7. Run the samples.

FIGURE 6 is the calibration curve of chromium (Cr) by atomic absorption ( A.A. ) analysis. TABLE 6 is the blank test for the leachate value of chromium (Cr) contaminated soil by EP TOXICITY TEST PROCEDURES.

## TABLE 6

## EP TOXICITY BLANK TEST of CHROMIUM ( Cr )

| Contaminated soil conceration ( ppm ) | Leachate value ( ppm ) | Percent of Cr fixed in soil (%) |
|---|---|---|
| 26.0 | 2.0 | 92 |
| 260.0 | 19.0 | 93 |
| 520.0 | 36.5 | 93 |
| *780.0 | 126.0 | 86 |

*780 : the leachout value 126.0 ppm is obtained by linear approach on Chromium-calibration curve ( FIGURE 6 )

## 3.Experiments of Chromium-contaminated soil:

Place the contaminated soil into microwave oven under the following conditions:

60:00 minutes at " HIGH " setting.

The microwave oven model which has been used for experiments is Sharp. R - 8580 A with frequency 2,450 MHz.

### (I) No additive:

There are two different sizes of reactors (beakers) used in the experiments. The one is 100 ml with S= 5.30 $cm^2$ ( S: exposed surface area ) and the other is 150 ml with S= 7.84 $cm^2$. Weigh 140 and 175 g of contaminated soils prepared as described before were used in this study. Nothing was placed on top of the soils. The beaker was put into the sand bed covered with aluminum foil on the side and bottom.
( Since aluminum foil reflects microwave energy, it allowed to absorb microwave energy only from the top of the beaker. )

The experiments are run at MW oven at conditions:

60:00 minutes at " HIGH " setting

### (II) -- 1. Additives : G.A.C.

There are two different sizes of reactors (beakers) used in the experiments. The one is 100 ml with S= 5.30 $cm^2$ ( S: exposed surface area ) and the other is 150 ml with S= 7.84 $cm^2$. Weigh 140 and 175 g of contaminated soils prepared as described before were used in this study. GAC was placed uniformly on top of the soils. The beaker was put into the sand bed covered with aluminum foil on the side and bottom. The experiments are run at MW oven at conditions:

60:00 minutes at " HIGH " setting

### (II) -- 2. Additives: iron wires

Iron wires were inserted into the contaminated soil to determine whether or not they can cause a deeper penetration of microwave energy absorption and how many iron wires were needed to achieve this. The chromium concentration of the contaminated soil was 260.0 ppm. The diameters of the iron wires were small, around 0.1 cm. By using different lengths of iron wires in soil (ID) and length exposed above the soil ( OL ), the effects of these parameters can be determined. The experiments were run under the following microwave oven conditions:

60:00 minutes at " HIGH " setting

After 60:00 minutes, the exposed beaker was cooled down to room temperature. The tests were set up to determine the leachability of the product. The E.P.A. leaching test gave a 5.0 mg/liter maximum level, for chromium (Cr) (From the table --- 40 CRF 261.30 --- the MAXIMUM CONCENTRATION OF CONTAMINANT FOR CHARACTERISTIC OF TOXICITY " D007 "). --- a value below E.P.A., drinking water criterion (not critical).

All the treated samples are analyzed by the EP TOXICITY TEST PROCEDURES. Atomic Absorption ( AA ) is the instrument to be used for analysis of leaching concentration of chromium.

FIGURE 11 (ID= 6.5 cm ), FIGURE 12 (ID= 7.5 cm ) and FIGURE 13 (ID= 10.0 cm ) give the reaction depth (RD) vs. iron-wire number for these three groups. The TABLE 10 gives the results of the experiments which include the Largest Penetration Depth (LPD), Reaction Range (RR), average Reaction Depth (RD), and leachate value for the number of iron wires between three and six.

The following are the definitions of RR, LPD and RD:

RR: The range where glass/ceramics formation occurred.
(in FIGURE 14, RR = M to N)

LPD: The largest vitrified depth which appears in a series of experiments.
(in FIGURE 14, LPD = the largest value of (M-N) )

RD: The average reaction depth among a series of experiments.

( Arithmetic average of (M-N) )

N: The shortest distance from the top of soil

M: The longest distance from the top of soil

## 2. Results and Discussion:

The final products are classified into two parts: one is the vitrified part named glass/ceramics formation, and the other is the non-vitrified part named soil formation. Most of the products are of the two parts mentioned above and some of them only consist of the non-vitrified part which means that dehydration happens only during reaction. Because of this result, the analytical results are also classified into glass/ceramics and soil parts.

The results of no-additive experiments are shown in TABLE 12. The results of additives with GAC are shown in TABLE 7, 8 and 9 and the results of additives with iron wires are shown in TABLE 10 and 11.

TABLE 6 shows that at low concentration of chromium, the soil immobilizes a certain amount of chromium. Only when the chromium concentration reaches a certain value the EP Leachate Test shows that chromium becomes bioavailable and has to be treated. This result gives a standard of blank leachate value from chromium-contaminated soil of Brunswick formation.

The concentration of contaminated soil is known as 26.0, 260.0 and 520.0 ppm. The standard value has to be compared with after MW treatment is different: 260.0 ppm of chromium in soil yield, just 19.0 ppm leachate value. This value is above the EP regulatory limitation for chromium in soil, so it must be treated to a value allowed by EP regulation. Can this remediation technique help to treat these leachate values to a acceptable status? It will be based on these leachate values shown in TABLE 6.

TABLE 7 shows the reaction conditions as the following:
Concentration of chromium : 260 ppm
Weight of GAC : at a range from 7.0 to 20.0 gm.
Height of GAC : at a range from 0.6 to 1.6 cm.
Volume of reactor : 150 ml.
Surface area of reactor : 7.84 $cm^2$
Reaction time : 60 min.

TABLE 8 shows the reaction conditions as the following:
Concentration of chromium : 260 ppm
Weight of GAC : at a range from 6.0 to 15.0 gm.
Height of GAC : at a range from 0.65 to 1.45 cm.
Volume of reactor : 100 ml.
Surface area of reactor : 5.30 $cm^2$
Reaction time : 60 min.

TABLE 9 shows the reaction conditions as the following:

Concentration of chromium : 260 ppm

Weight of GAC : 10.0 gm.

Height of GAC : 1.3 cm.

Volume of reactor : 100 ml.

Surface area of reactor : 5.30 $cm^2$

Reaction time : at a range from 10 to 60 min.

All of the TABLES 7, 8 and 9 show the results of vitrification with GAC. Results of TABLE 7 are shown graphically in FIGURE 7 and 8. In FIGURE 7, the ratios of soil to GAC are plotted against the reacted depth of soil vitrified, while in FIGURE 8, the heights of GAC over soil are plotted vs the reacted depth of soil vitrified. Results of TABLE 8 are shown in FIGURE 9 and 10. These two tables, TABLE 7 and 8, differ in the volume of reactors (150 and 100 ml) used. TABLE 9 shows the results of vitrification of chromium contaminated soil with variable time ( from 10 to 60 minutes ) and 10 g of GAC as additives.

## The Results of TABLES 7, 8, and 9 - with GAC as additives

- FIGURE 7 and 9 show that a break of penetration occurs at the ratio of soil weight to GAC weight around 17.5 gm.
- FIGURE 8 and 10 show that a break of penetration occurs at the height of GAC around 0.75 to 0.90 cm.

- After the break, the ones with the larger volume ( 150 ml ) and surface area (7.84 $cm^2$) have a deeper reacted depth than the ones with smaller volume (100 ml) and surface area (5.30 $cm^2$).
- TABLE 9 shows the vitrification occurs at 40 minutes.
- All the vitrified parts have leachate values below the EP regulation for chromium, but not all non-vitrified parts.

Both TABLEs 10 (group Iron-Wire) and 11 show the results of vitrification with iron wires. Results of group iron-wire are shown graphically in FIGURES 11, 12 and 13. These three figures differ in the inner depth (ID) : 6.5, 7.5 and 10.0 cm respectively. The reaction conditions are given as the following :

Concentration of chromium : 260 ppm
Numbers of iron wires : from one to six
Volume of reactor : 100 ml.
Surface area of reactor : 5.30 $cm^2$
Reaction time : 60 min.

TABLE 11 shows the results of vitrification of chromium contaminated soil with four iron wires and variable time (from 10 to 60 minutes)

The Results of TABLE 10 and 11 - with four iron wires as additives

- A break of penetration occurs at three iron wires. ( see FIGURE 11, 12 and 13 ).
- In TABLE 10 and FIGURE 13 ( ID = 10 cm ), there a 9.3 cm of vitrification depth occurs. This shows that iron wires are capable of inducing MW energy to penetrate deeper into the soil.
- In TABLE 11, vitrification occurs at 40 minutes ( such as TABLE 9 ).
- All the vitrified parts have leachate values below the EP regulation for chromium, but not all non-vitrified parts.

TABLE 12 shows the results of vitrification of chromium contaminated soil without any additives, but with variable time ( from 10 to 60 minutes ).

The Results of TABLE 12 - without any additives

- In one case, there is vitrification.
- The leachate value of the vitrified one is below the EP regulation, but it is not true for all the non-vitrified parts.
- A certain amount of chromium is immobilized in soils without vitrification happening.

In TABLE 12 shows that, in one case, vitrification was achieved without any additives. This experiment shows that, at least under certain conditions, vitrification can be achieved without any additives.

The most important phenomena can be found from TABLE 12 is that chromium can be immobilized in soils without vitrification. The leachate value is distributed from 3.5 to 8.5 for a chromium-contaminated soil of 260 ppm. Compared with the original leachate data, a large amount of chromium is immobilized in soils. Before vitrification, only dehydration occurs. Is this meant that immobilization of chromium needs dehydration process only?

Theoretically, silica/clay soils do not absorb too much microwave energy. There should not be any vitrification in absence of additives, but in TABLE 12, one of the data shows that vitrification did happen without any additives. Why does the one with no additives absorb microwave energy and cause vitrification? And, in case the vitrification can happen without any additive, why is the additive needed any more? The reason can be given as the followings:

(a). No additives:

Silica/clay soil absorbs little microwave energy at the beginning, then the temperature rises up a little. At the same time, the dielectric constant value increases and, also, the loss tangent increases too. Because the dielectric constant and loss tangent is increased, the silica/clay soil can absorb more microwave energy, then it causes dielectric constant and loss tangent increased. The dielectric constant and loss tangent increases little by little, meanwhile the silica/clay soil absorbs more microwave energy little by little. Finally, it becomes a microwave energy absorber.

(b). Additives of GAC and iron wires:

The additives are used to absorb more microwave energy, then transfer their heat to silica/clay soil. They shorten the relaxation time. Therefore, the additives of GAC and iron wires make a short time to achieve immobilization of the chromium-contaminated soil. The following questions can be the suggestions for the further studies:

1. How does the dehydration process affect the immobilization of chromium in soils?
2. What caused the vitrification ?
3. Which molecules were heated ?
4. How was the vitrification formed in MW field ?
5. What are the bonding-structures of the chromium in soils?

## TABLE 7

Tests of chromium contaminated soil with additives: GAC

Experimental group: Cr-A

Surface area : 7.84 cm$^2$

Beaker size : 150 ml

Reaction time: 60 minutes

| EXPT. # | Cr (ppm) initial | Depth (cm) | Leachate (ppm) (glassy part) | Leachate (ppm) (non-glassy part) |
|---|---|---|---|---|
| BLANK-1 | 260 | ----- | 19 (blank) | 19 (blank) |
| BLANK-2 | 780 | ----- | 126 (blank) | 126 (blank) |
| A - 01 | 260 | 0.0 | --------- | 2.45 |
| A - 02 | 260 | 0.5 | < 1.0 | 2.79 |
| A - 03 | 260 | 0.7 | < 1.0 | 1.97 |
| A - 04 | 260 | 3.5 | < 1.0 | 3.21 |
| A - 05 | 260 | 3.4 | < 1.0 | 2.55 |
| A - 06 | 260 | 4.0 | < 1.0 | 1.89 |
| A - 07 | 260 | 4.0 | < 1.0 | 1.76 |
| A - 11 | 780 | 3.7 | < 1.0 | 22.8 |

TABLE 8

Tests of chromium contaminated soil with additives: GAC

Experimental group: Cr-B

Surface area : 5.30 $cm^2$

Beaker size : 100 ml

Reaction time: 60 minutes

| EXPT. # | Cr (ppm) initial | Depth (cm) | Leachate (ppm) (glassy part) | Leachate (ppm) (non-glassy part) |
|---|---|---|---|---|
| BLANK-1 | 260 | ----- | 19 (blank) | 19 (blank) |
| BLANK-2 | 780 | ----- | 126 (blank) | 126 (blank) |
| B - 01 | 260 | 0.2 | < 2.0 | 2.45 |
| B - 02 | 260 | 0.5 | < 1.0 | 2.77 |
| B - 03 | 260 | 3.7 | < 1.0 | 1.94 |
| B - 04 | 260 | 3.5 | < 1.0 | 2.33 |
| B - 05 | 260 | 3.5 | < 1.0 | 3.17 |
| B - 06 | 260 | 3.6 | < 1.0 | 2.12 |
| B - 07 | 260 | 3.6 | < 1.0 | 1.86 |

*

Depth: the depth of the vitrified (glassy) part in cm.

Glassy part: the ceramic/glass formation part.

Non-glassy part: the soil formation part.

## TABLE 9

Tests of chromium contaminated soil with:

additives - 10.0 gm of GAC and variable time

( Contaminated soil with 260 ppm chromium )

| sample parts minutes | vitrified part leachate (ppm) | red part leachate (ppm) | black part leachate (ppm) | original part leachate (ppm) |
|---|---|---|---|---|
| 10:00 | ---- | ---- | ---- | 18.5 |
| 20:00 | ---- | ---- | ---- | 17.0 |
| 30:00 | ---- | ---- | ---- | 15.5 |
| 40:00 | < 1 | ---- | ---- | 19.5 |
| 50:00 | < 1 | ---- | 6.5 | 14.5 |
| 60:00 | < 1 | ---- | 2.5 | 16.0 |

## TABLE 10

### Tests of chromium contaminated soil with additives: IRON WIRES

Experimental group: IRON-WIRE

Iron wire numbers : 3 to 6

Reaction time : 60 minutes

| ID (cm) | 6.5 | 7.5 | 10.0 |
|---|---|---|---|
| OL (cm) | 1.0<br>1.5<br>2.5 | 1.0<br>1.5<br>2.5 | 1.0<br>1.5<br>2.5 |
| Cr concentration of soil | 260 ppm | 260 ppm | 260 ppm |
| Iron-wire numbers | 3 ~~ 6 | 3 ~~ 6 | 3 ~~ 5 |
| LPD (cm) | 7.0 | 7.7 | 9.3 |
| RR (cm~cm) | 0.1~~7.1 | 0.2~~8.1 | 0.1~~9.4 |
| RD (cm~cm) | 6.6 | 7.2 | 8.6 |

-- glass/ceramics formation --

| | | | |
|---|---|---|---|
| Leachate value ( ppm ) | < 1. | < 1. | < 1. |

-- mixed soil formation --

| | | | |
|---|---|---|---|
| Leachate value ( ppm ) | 2.~~3. | 2.~~4. | 1.~~4. |

TABLE 11

Tests of chromium contaminated soil with:

additives - four iron wires and variable time

( with 6.5 cm inner depth and 2.0 cm outer length )

( Contaminated soil with 260 ppm chromium )

| sample parts minutes | vitrified part leachate (ppm) | red part leachate (ppm) | black part leachate (ppm) | original part leachate (ppm) |
|---|---|---|---|---|
| 10:00 | ~~~~ | ~~~~ | ~~~~ | 21.0 |
| 20:00 | ~~~~ | ~~~~ | ~~~~ | 18.0 |
| 30:00 | ~~~~ | 9.5 | ~~~~ | 16.5 |
| 40:00 | < 1 | 7.0 | ~~~~ | 13.5 |
| 50:00 | < 1 | 2.5 | ~~~~ | 16.0 |
| 60:00 | < 1 | 4.5 | ~~~~ | 15.0 |

# TABLE 12

Tests of chromium contaminated soil with:

no additive and variable time

( Contaminated soil with 260 ppm chromium )

| sample parts minutes | vitrified part leachate (ppm) | red part leachate (ppm) | black part leachate (ppm) | original part leachate (ppm) |
|---|---|---|---|---|
| 10:00 | ~~~~ | ~~~~ | ~~~~ | 18.5 |
| 20:00 | ~~~~ | ~~~~ | ~~~~ | 19.5 |
| 30:00 | ~~~~ | ~~~~ | ~~~~ | 16.0 |
| 40:00 | ~~~~ | 8.5 | ~~~~ | 14.5 |
| 50:00 | ~~~~ | 3.5 | ~~~~ | 19.0 |
| 60:00 | < 1 | 4.5 | ~~~~ | 15.5 |
| 60:00 | ~~~~ | 6.5 | ~~~~ | 16.5 |
| 60:00 | ~~~~ | 8.0 | ~~~~ | 18.0 |

## 3. Conclusion:

Although the detail reaction mechanism and bonding-structure of chromium and soil are not clear, it is clear that to effect the immobilization of chromium in soils it is not necessary to vitrify the soils. A great cost-saving can be effected on scale-up for remediation of chromium-contaminated soil because less energy is needed to cause immobilization than to cause vitrification. The calculations of efficiency of vitrification and dehydration which are presented here are approximations, but, obviously, it is technically feasible to stabilize chromium in soil by the application of microwave energy.

## G. FUTURE WORK

The bench-scale studies yielded an unexpected result. It was observed that chromium could be immobilized even if the soils were not vitrified. Apparently the nature of the chromium ion changes as a result of dehydration in an irreversible manner to form an ionic species or a new crystalline state which immobilizes the chromium. Since the effect is beneficial because energy costs are decreased, it is important to determine the nature of the transformation of the chromium. That information can lead to strategies to effect the chromium ion transformation in the most cost-effective way. It is proposed that one way in which this information can be obtained is by X-ray studies and scanning electron microscopy studies of the soil as the changes occur from the leachable initial state to the immobilization state, and, finally, to the vitrification state.

To scale-up the process, it is necessary to study it on a pilot plant scale. The following is a sketch of a proposed pilot plant:

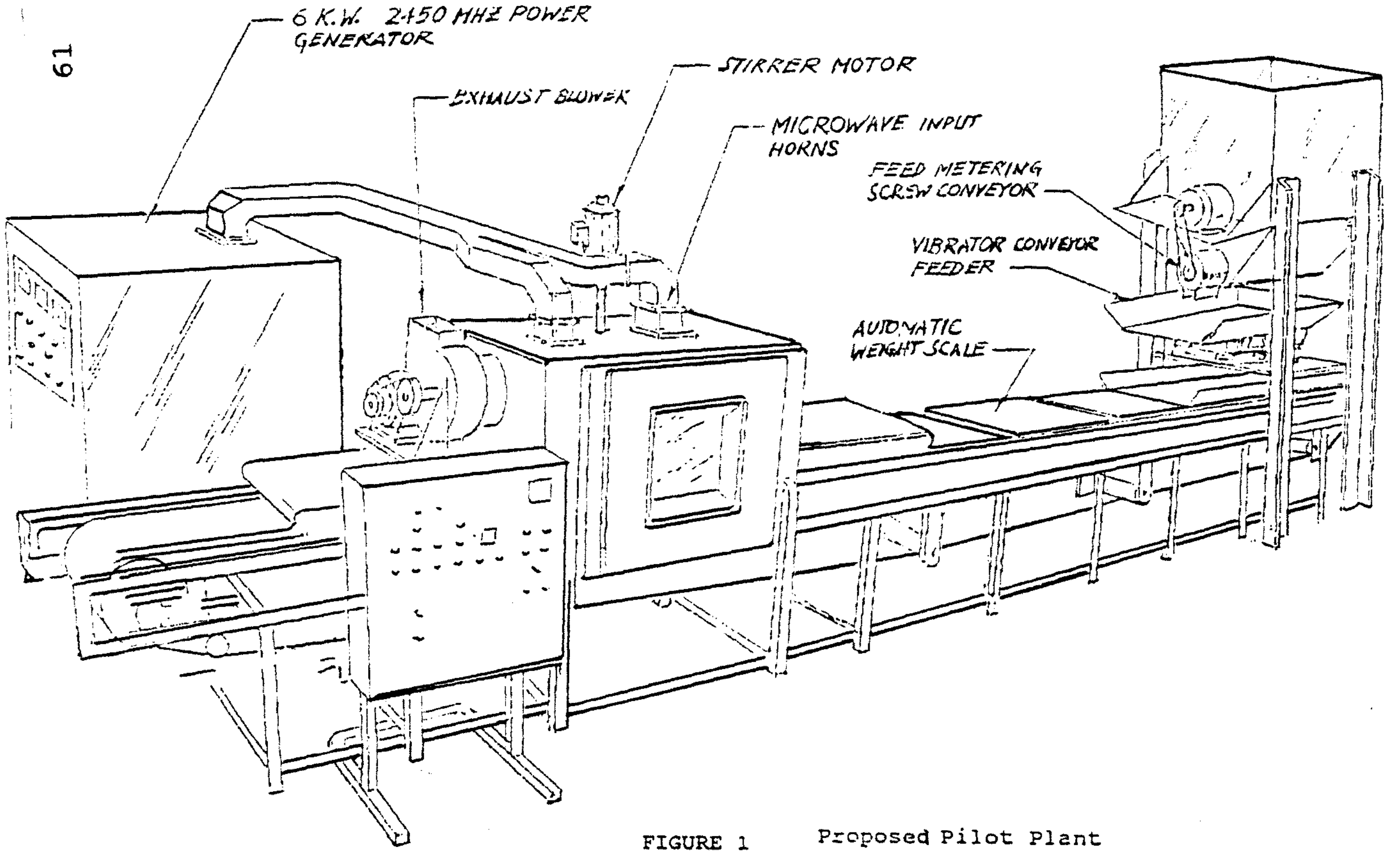
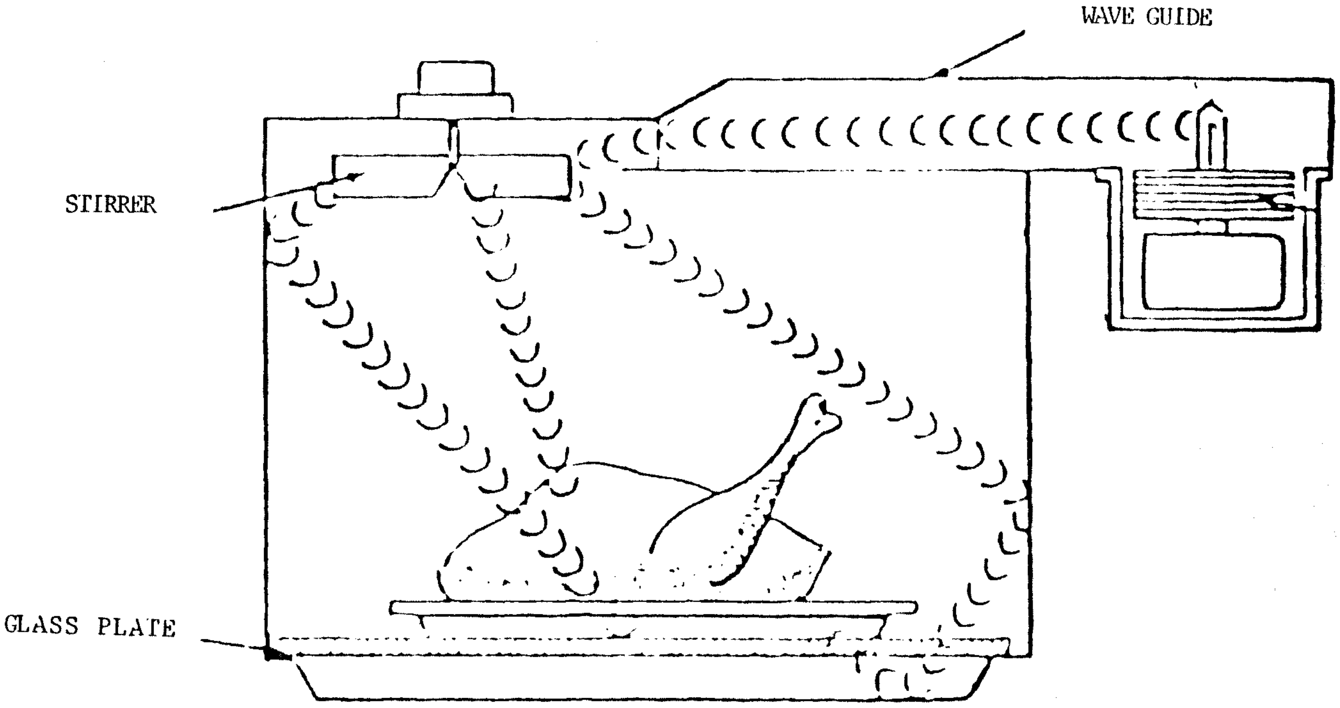


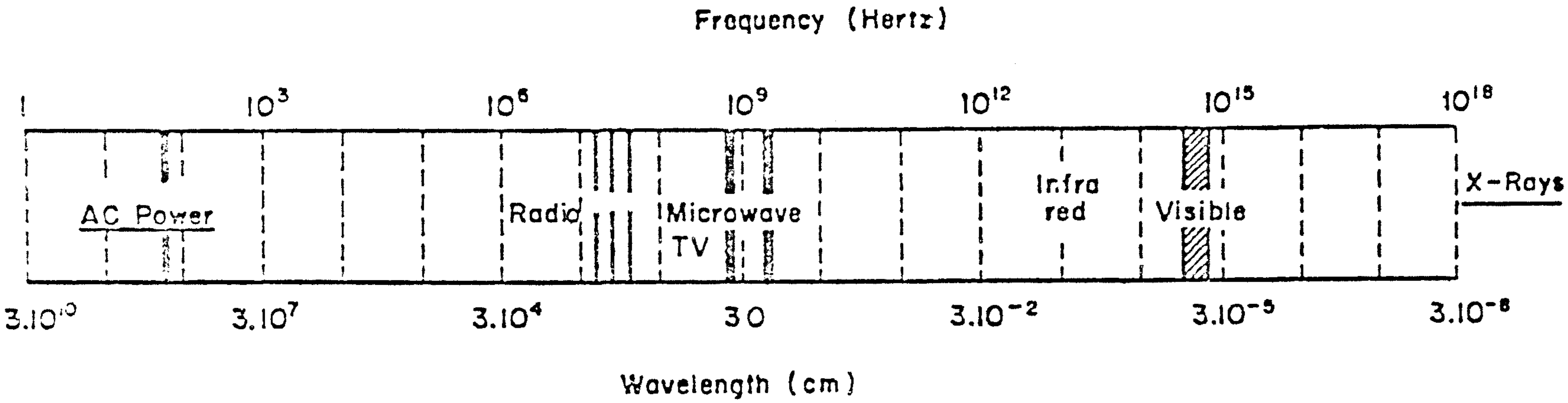
FIGURE 1 Proposed Pilot Plant

The soil is fed from the hopper by a screw-conveyor onto vibrating pan, and, then, it is fed to the conveyor belt. The soil is continuously weighed on the belt; it enters a 50 $ft^3$ cavity with a 6 kW ( 6,000 watts ) microwave radiation source. It is believed that studies on such a system will provide the parameters needed for scale up.



Microwave oven

FIGURE 2



The Electromagnetic Spectrum.

FIGURE 3

(H) vs (V/t), at constant (S)

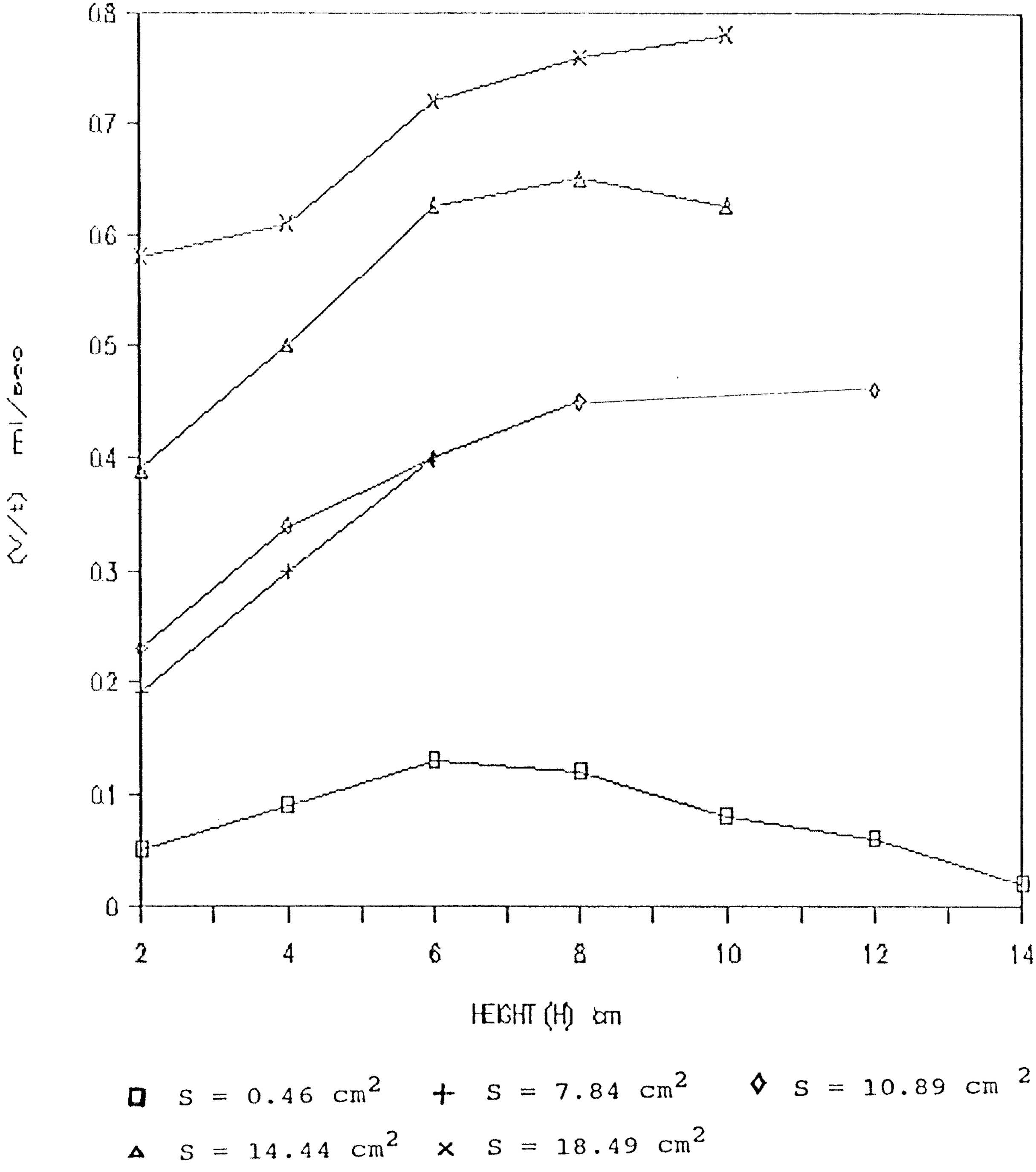


FIGURE 4

( S ) vs ( V/t ), at constant ( H )

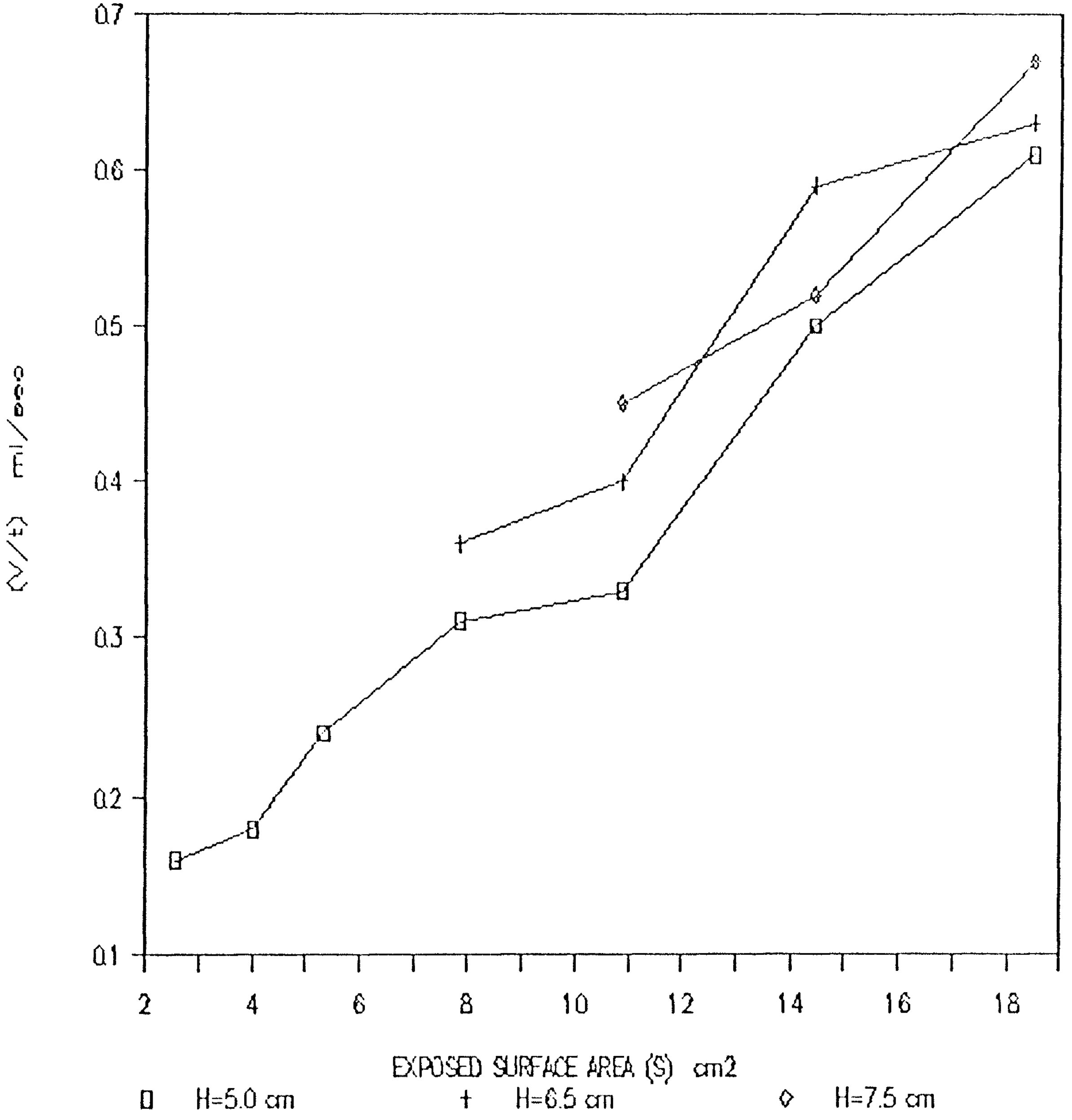


FIGURE 5

(S) vs (V/t), at constant (V)

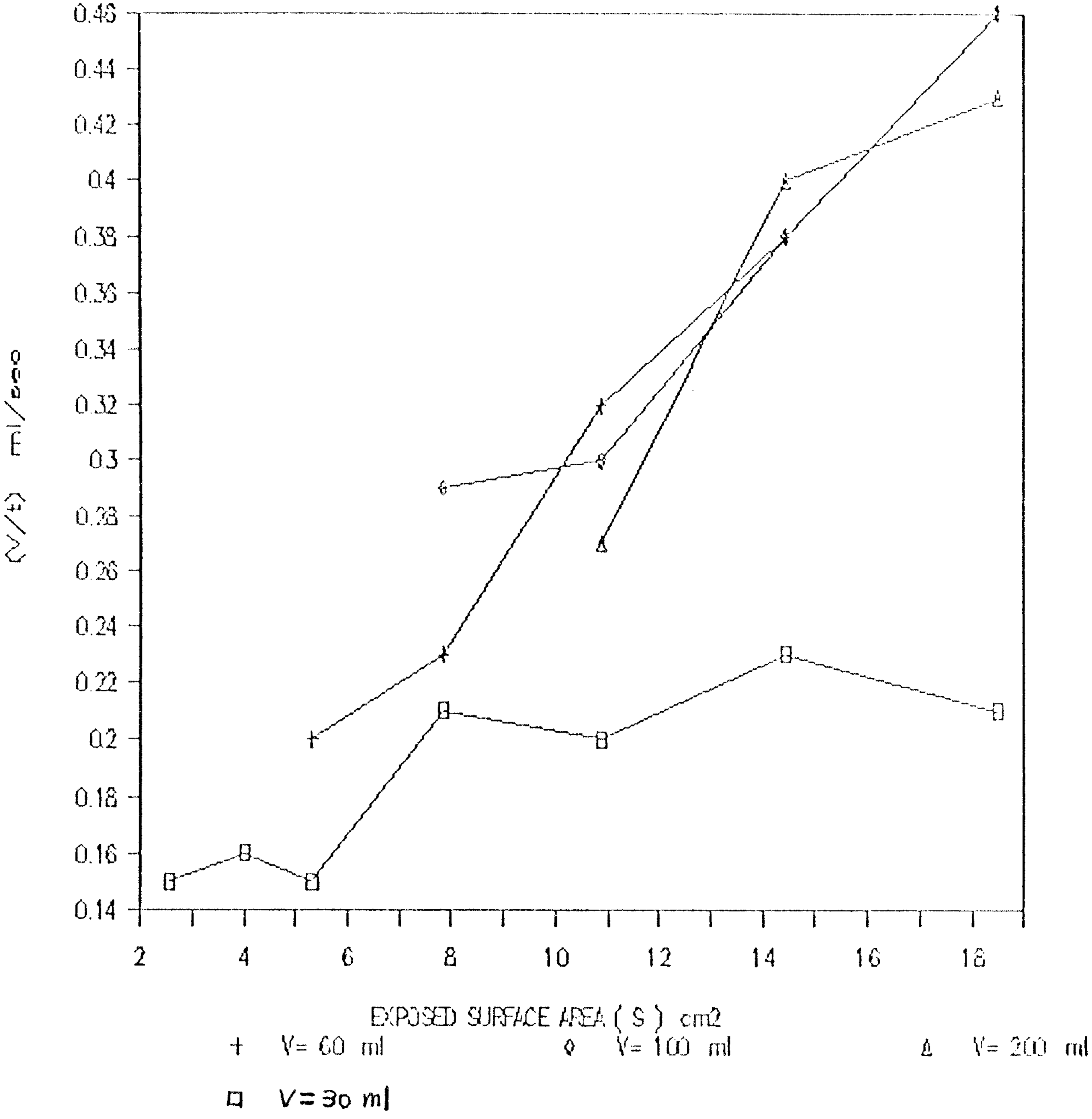
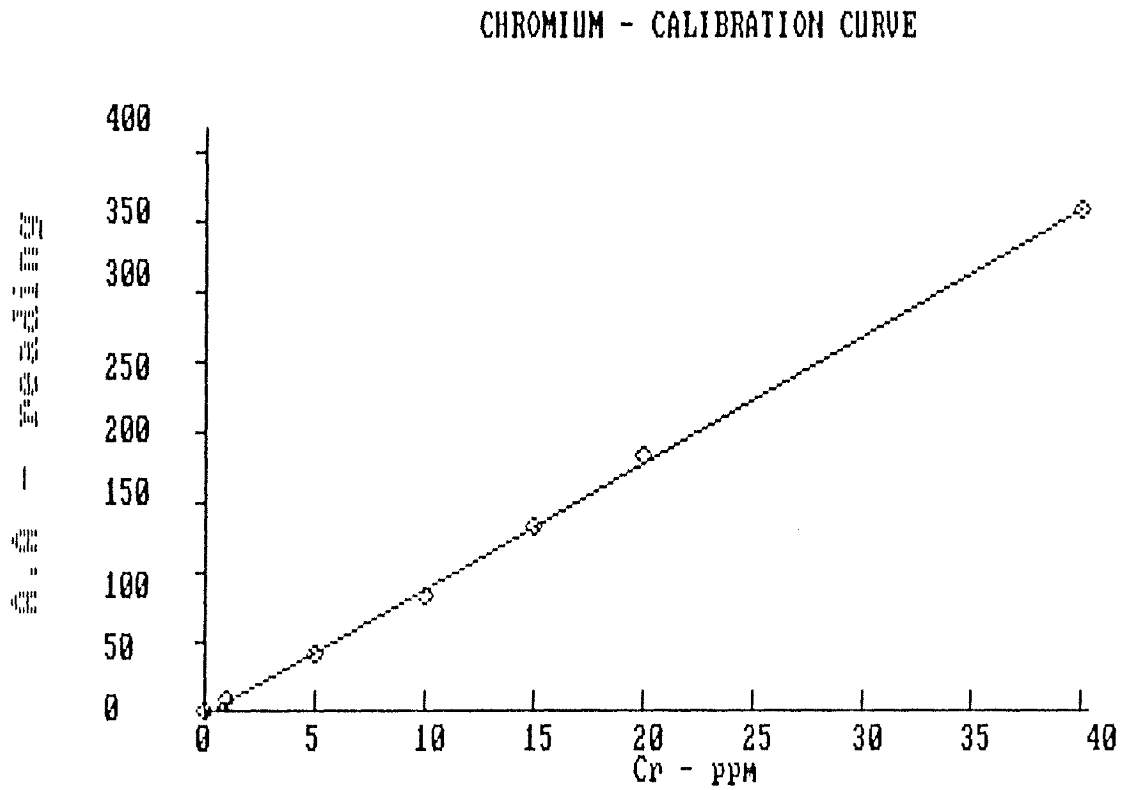


FIGURE 6



CHROMIUM - CALIBRATION CURVE

| POINT | X | Y |
|---|---|---|
| 1 | 0 | 0 |
| 2 | 1 | 8 |
| 3 | 5 | 41 |
| 4 | 10 | 82 |
| 5 | 15 | 134 |
| 6 | 20 | 182 |
| 7 | 40 | 358 |

Slope = 9.022261 +/- .1025366
Intercept = -2.289385 +/- 3.504294
Correlation = .9996772
Calculated on points 1 TO 7

FIGURE 7

VITRIFED HEIGHT vs RATIO SOIL TO GAC

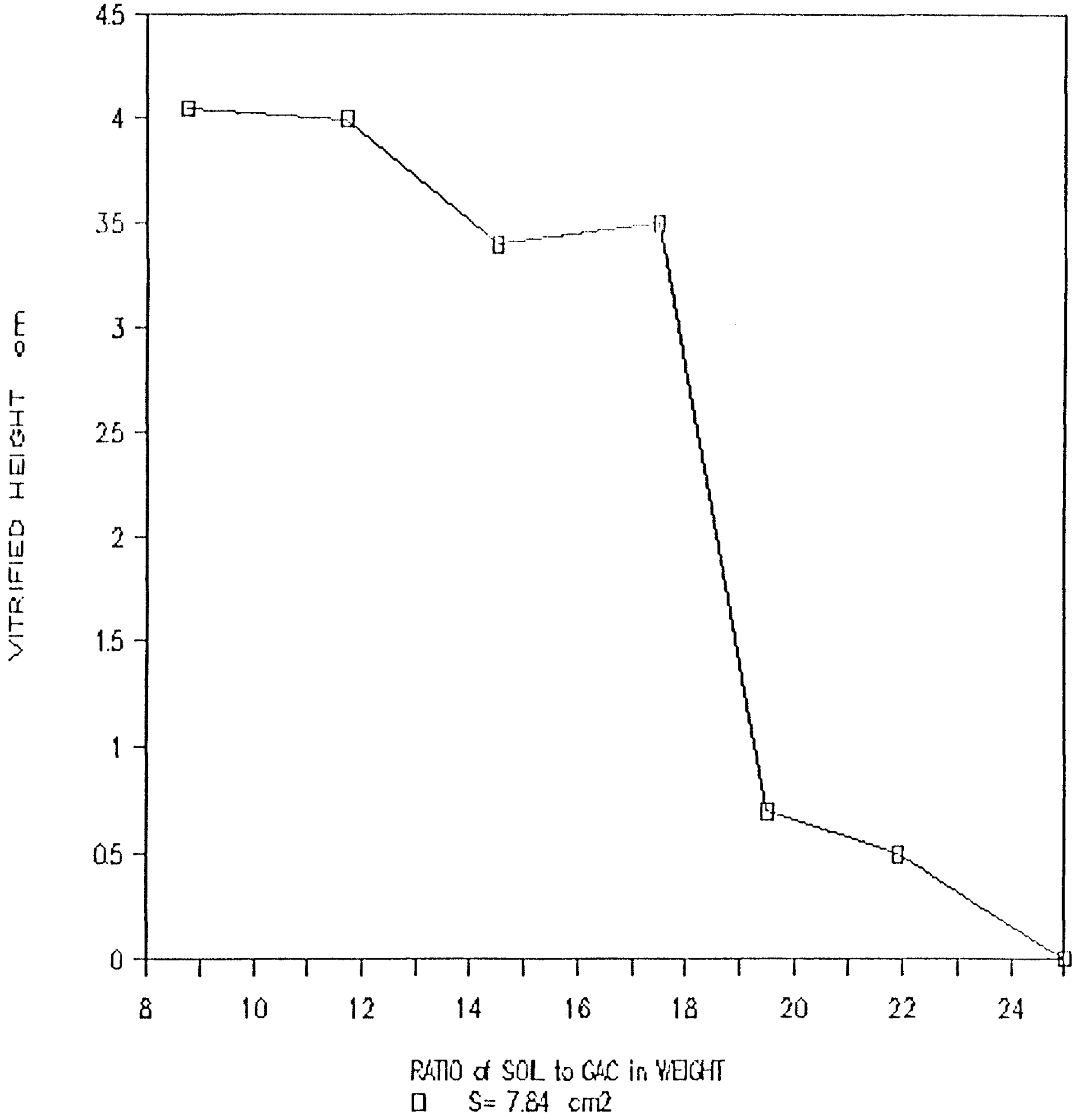


FIGURE 8

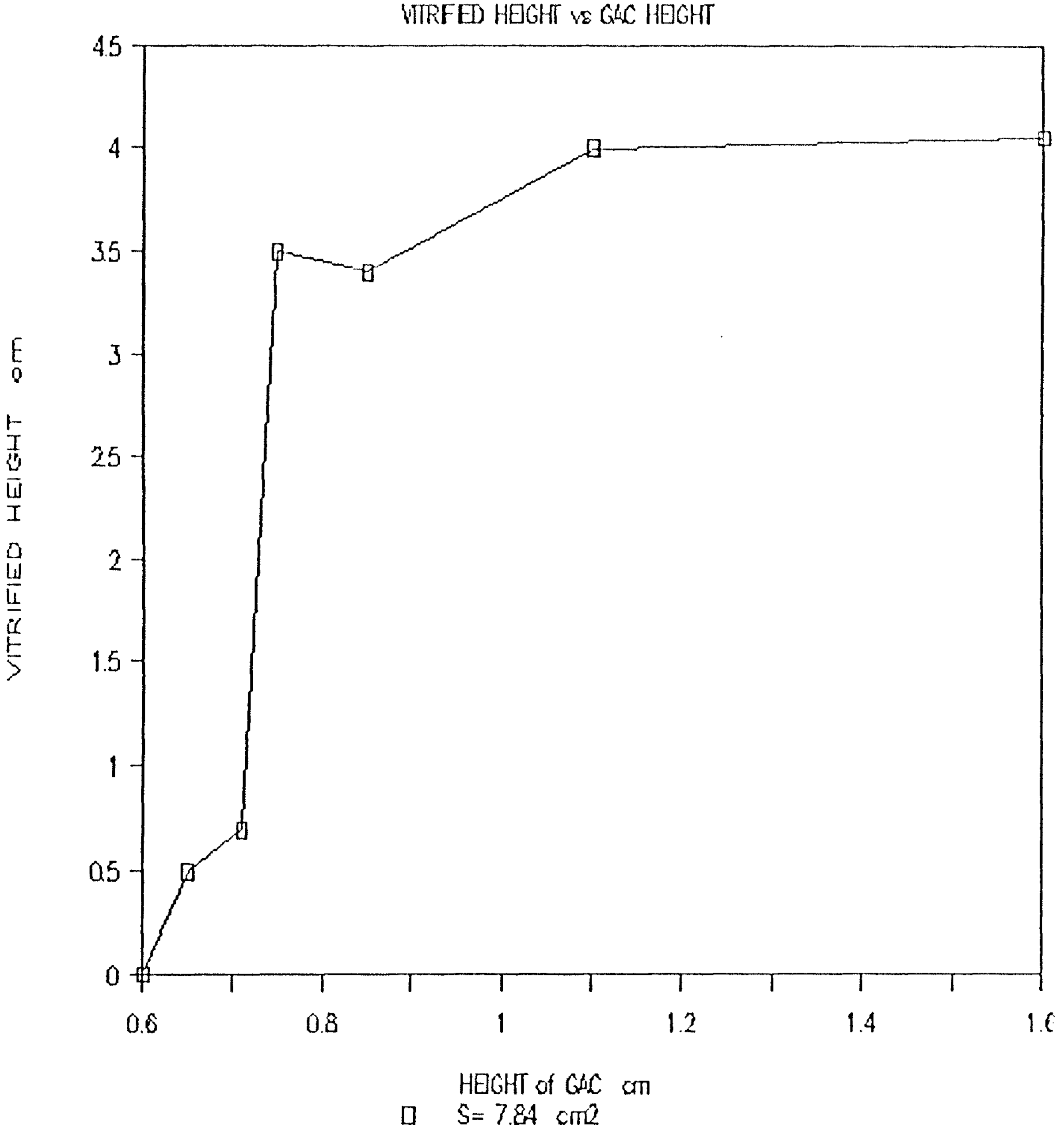

VITRFED HEIGHT vs GAC HEIGHT
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
VITRIFIED HEIGHT cm
0.6
0.8
1
1.2
1.4
1.
HEIGHT of GAC cm
□ S= 7.84 cm2

FIGURE 9

VITRIFIED HEIGHT vs RATIO SOIL TO GAC

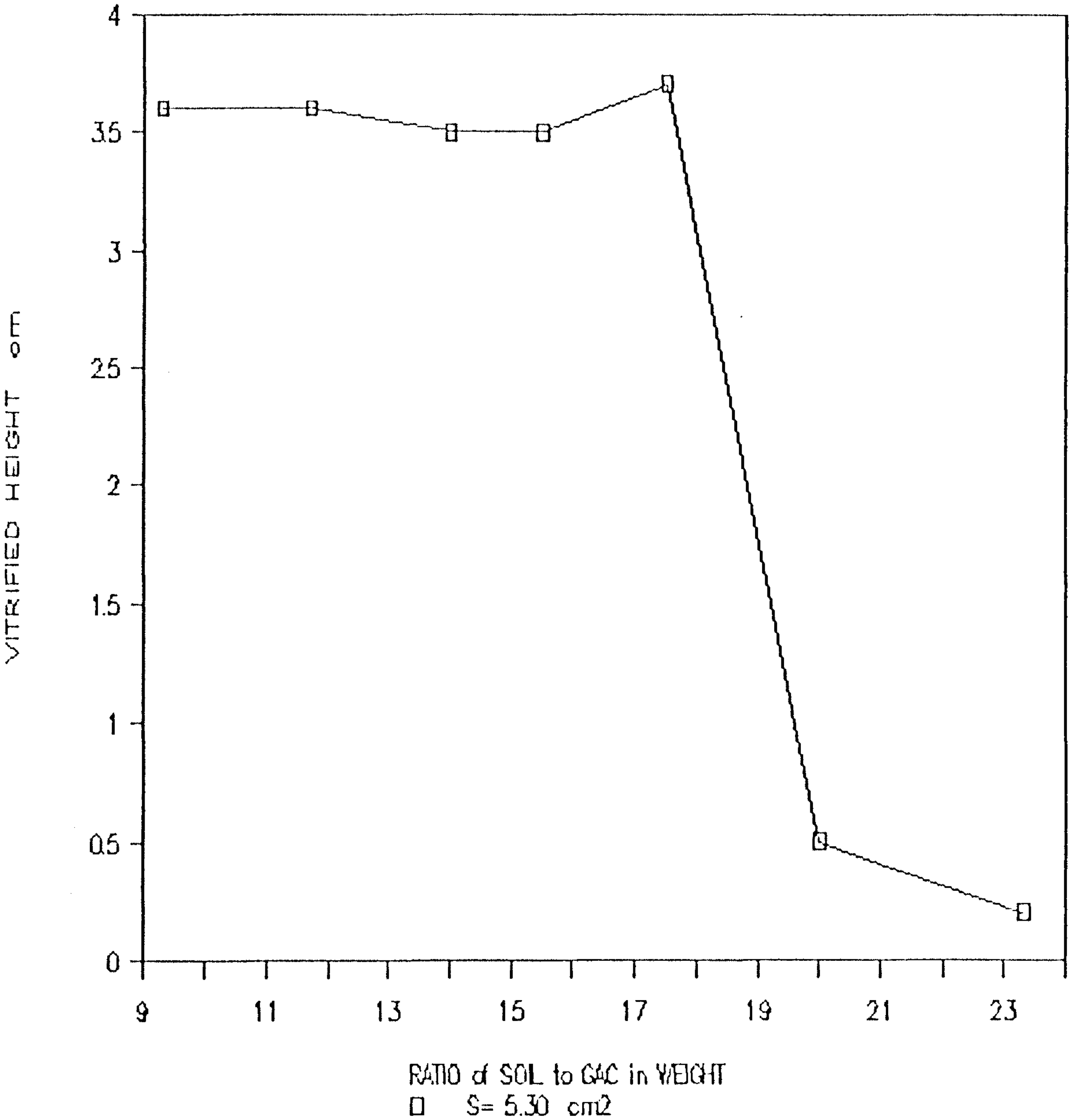
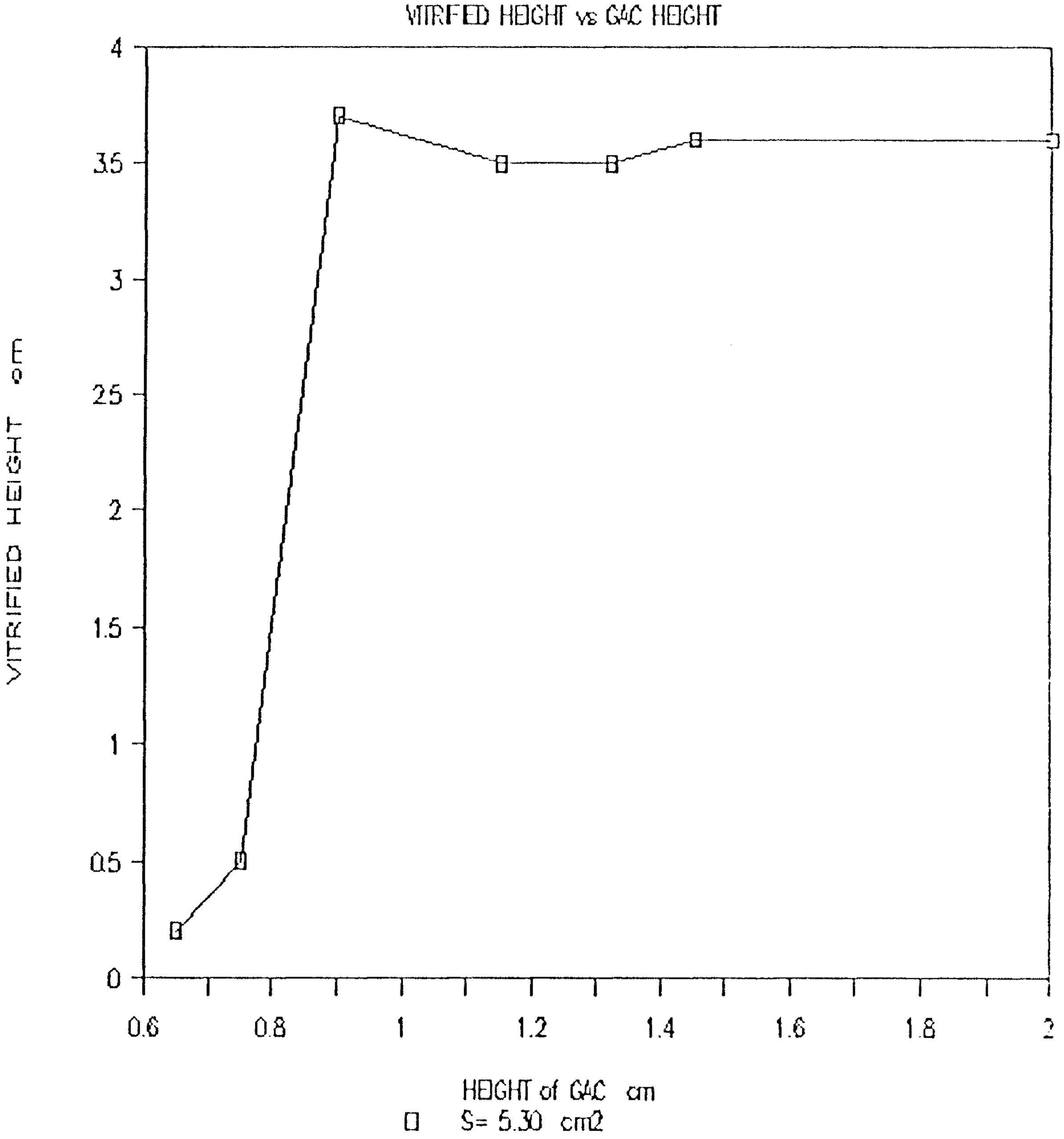


FIGURE 10



VITRFED HEIGHT vs G4C HEIGHT

# FIGURE 11

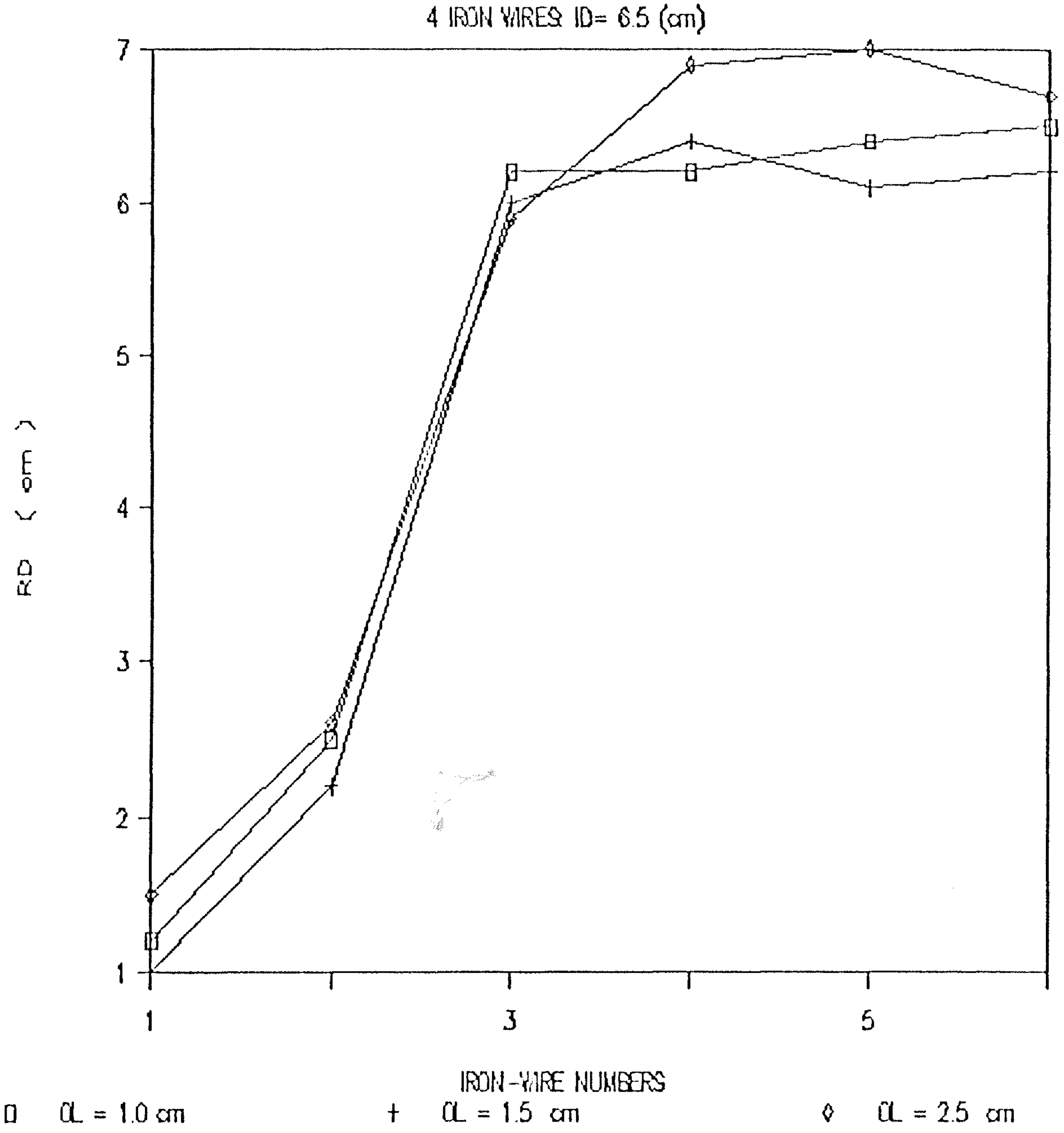

4 IRON WIRES ID= 6.5 (cm)
RD ( cm )
7
6
5
4
3
2
1
1
3
5
IRON-WIRE NUMBERS
□ OL = 1.0 cm
+ OL = 1.5 cm
◊ OL = 2.5 cm

FIGURE 12

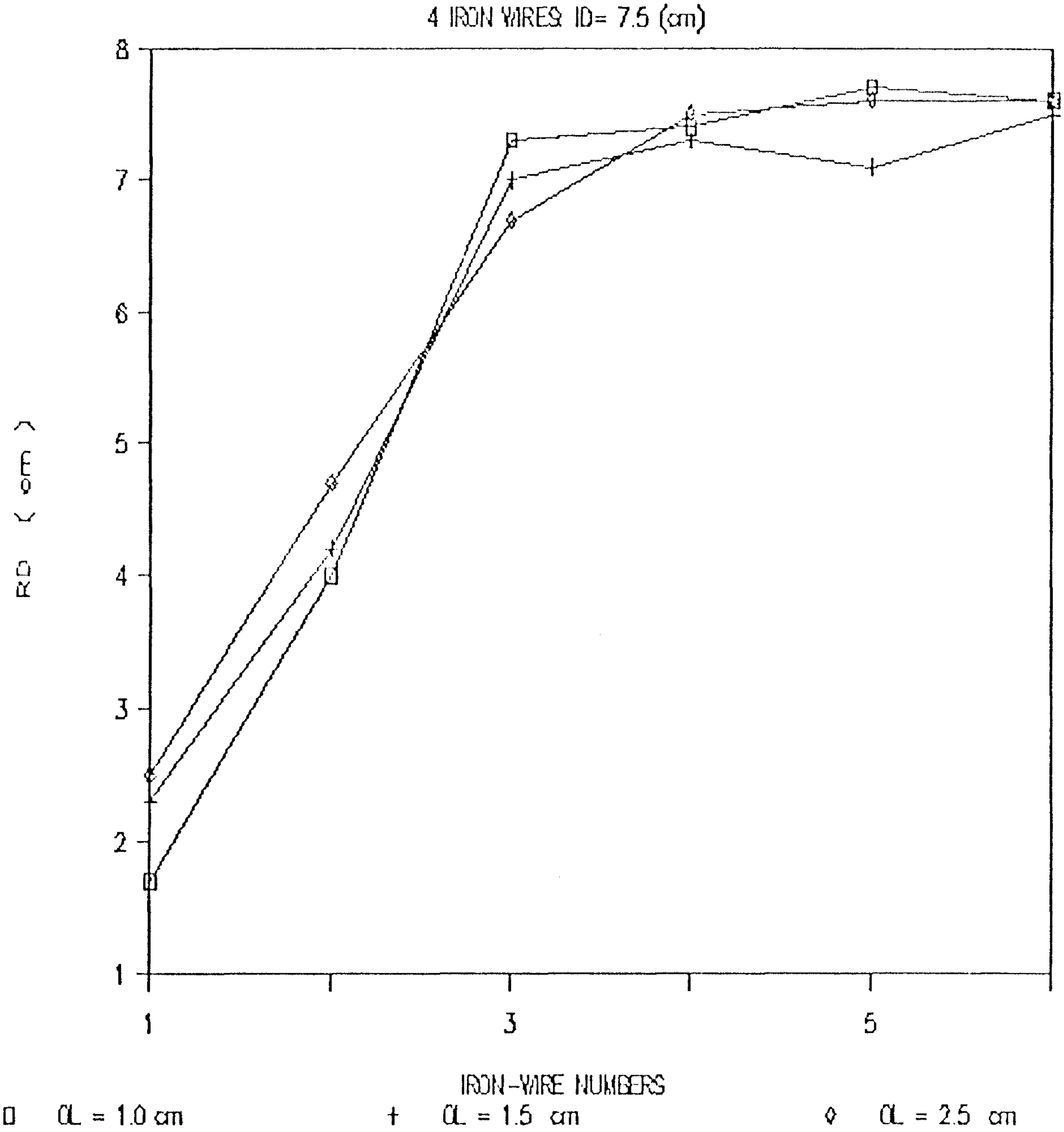
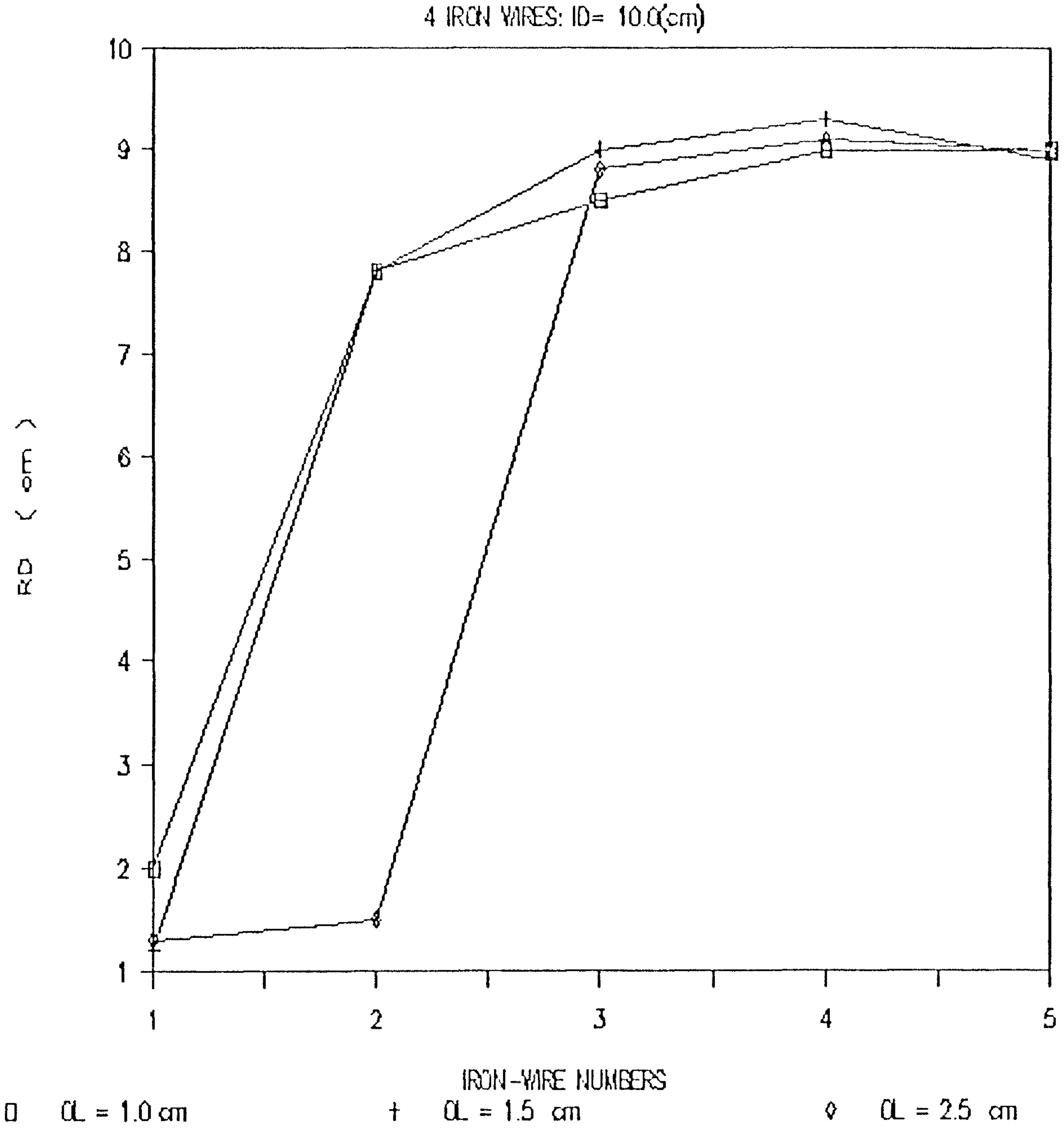

4 IRON WIRES ID= 7.5 (cm)
RD (cm)
8
7
6
5
4
3
2
1
1
3
5
IRON-WIRE NUMBERS
□ CL = 1.0 cm
+ CL = 1.5 cm
◊ CL = 2.5 cm

FIGURE 13


4 IRON WIRES: ID= 10.0(cm)
RD (cm)
10
9
8
7
6
5
4
3
2
1
1
2
3
4
5
IRON-WIRE NUMBERS
□ OL = 1.0 cm
+ OL = 1.5 cm
◊ OL = 2.5 cm

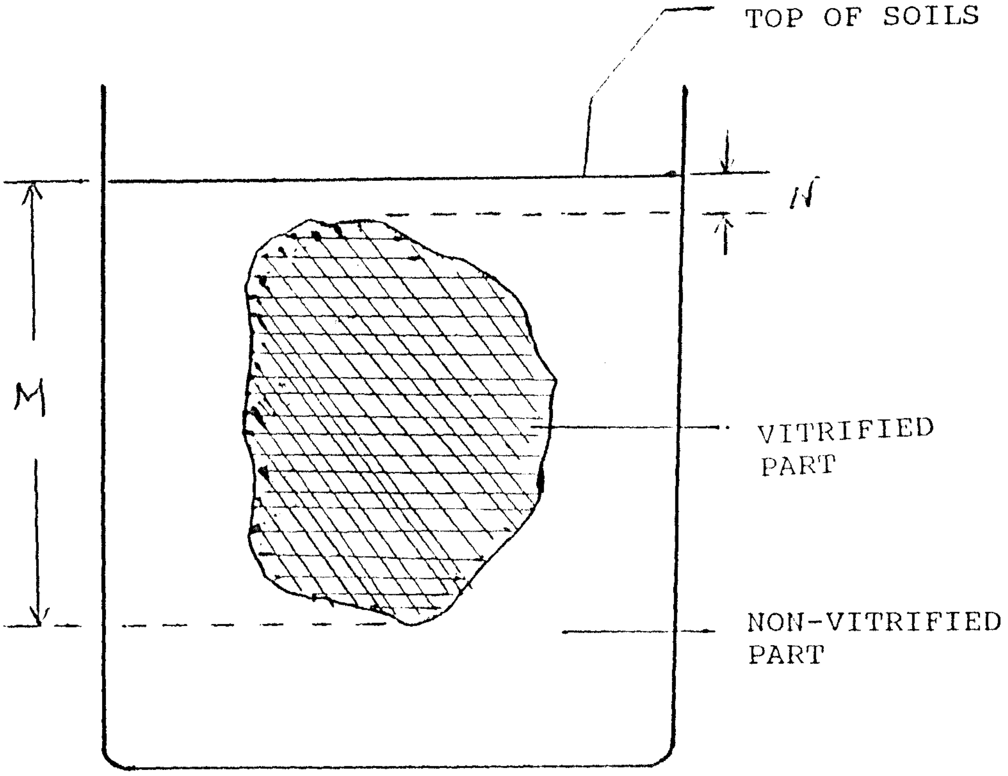


FIGURE 14

Pictorial definition of 'M' and 'N' for soil vitrification studies

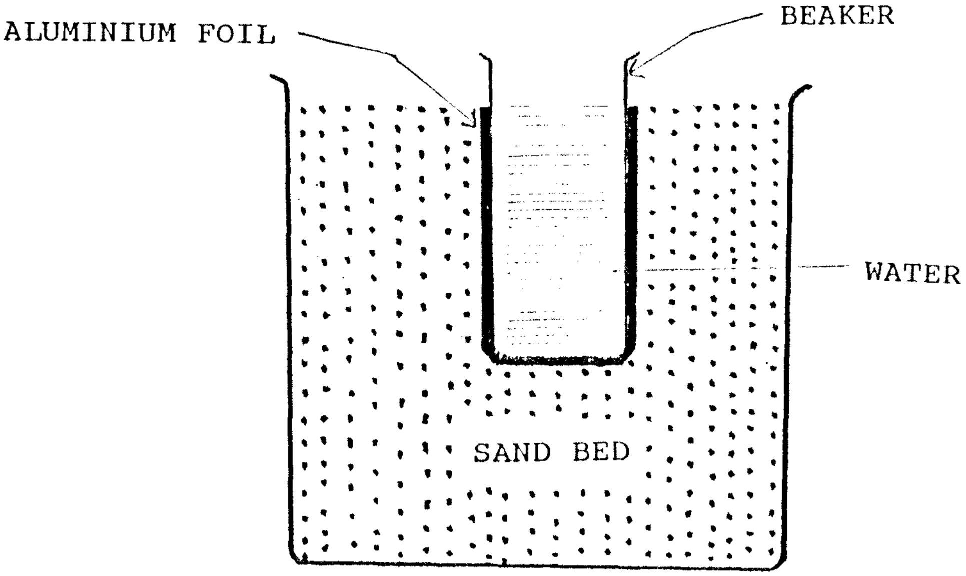


FIGURE 15

Experimental set-up for the measurement of different parameters using water as a load

Exposed surface area ( S )

Height of water ( H )

Volume of water ( V )

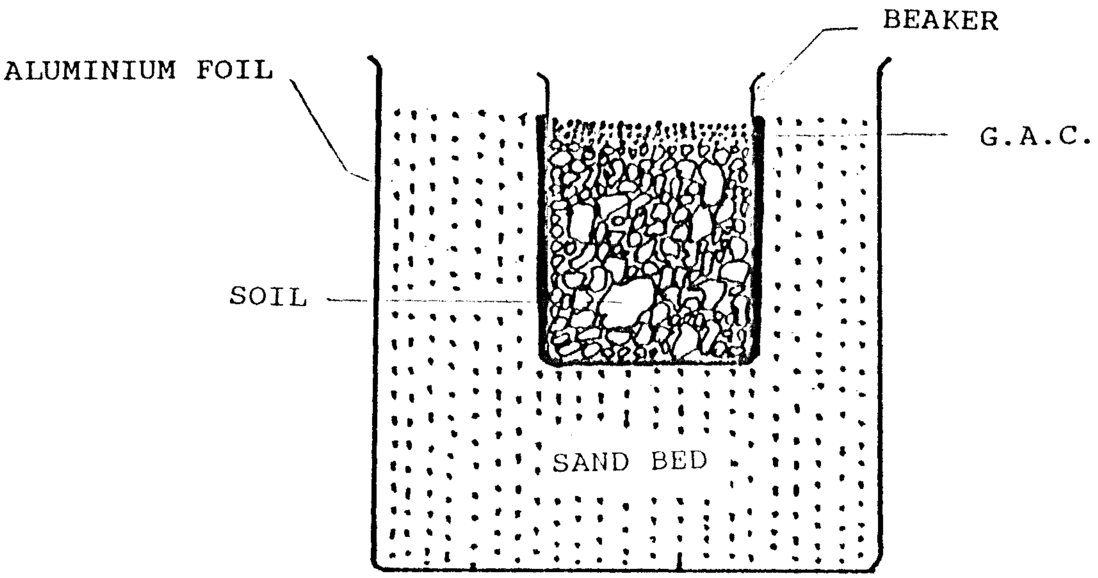


FIGURE 16

Vitrification of chromium contaminated soil

with GAC only

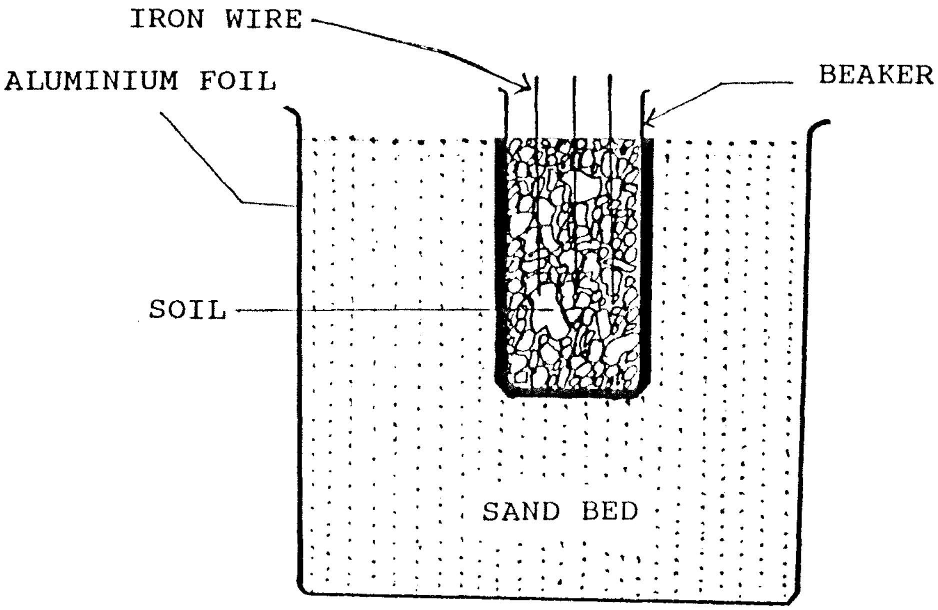


FIGURE 17

Vitrification of chromium contaminated soil

with IRON WIRES only

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