Microwaves in Soil Remediation from VOCs. 1: Heat and Mass Transfer Aspects

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A novel technique presented performs in situ remediation of soils contaminated by volatile organic compounds (VOCs) based on the use of electromagnetic fields for heating operations. Attention is focused on heat and mass transfer occurring in porous-moisturized media like a soil matrix. The microwave induced steam distillation process is investigated. Measurements are reported of temperature, humidity, residual contaminant concentration, and permittivity during the process. The crucial role is elucidated that the changes of the dielectrical properties of the soil matrix play on the electromagnetic field propagation. A mathematical model of the remediation process relating all the parameters above is proposed and validated.

Introduction

Increasing attention is drawn by the remediation of contaminated sites due to both focusing of citizens on the subject and the major concern that governments show towards the recovery of industrial areas to new public or productive uses.

Many pollution sources can be identified in previous industrial installation or waste disposal sites, as exposed from a process performed on the site or from the accidental release of polluting substances in the environment. Also, leaks or disasters during oil transportation result in tremendous pollution of the sites involved (see harbors or beaches).

As a matter of fact, selecting the most appropriate methodology of remediation requires accurate knowledge of the kinds of contaminant, soil chemical properties, physical and geological characteristics, as much as site topography. Each of the methods above offers both advantages and drawbacks to being the number of parameters, which are accounted to be significantly large. See the required time, cost, efficiency, safety, and environmental impact. Moreover, the extent of remediation will affect the final choice, that is, whether the site has to be completely remedied or the contamination has only to be confined.

In the following a short review of the most applied methodologies to remedy a polluted soil is presented. The attention has been focused on the techniques adopted to remove volatile organic compounds (VOCs), from a soil matrix.

Decontamination treatments

A number of techniques methodologies have been developed to remedy polluted soils, ranging from physico-chemical to thermal and biological processes, either to be adopted *in situ* or not. When possible, *in situ* treatments are preferred since remediation is applied *in loco* without auxiliary operations (soil excavation and conveyance). On the contrary, *ex situ* operations are accomplished by mechanical removal of contaminated layers followed by off-line treatments. These kinds of treatments are characterized by both a high cost due to the often enormous amount of soil to be moved and a high hazardousness of the carried material.

Physico-chemical treatments can be applied when relatively easy separation of contaminant from soil matrix is possible. *In situ* techniques make pollutants mobile by using a medium (water, air, steam, and so on) and then extract the medium out of the soil. For this technique, the soil matrix has to be permeable and pollutants must have interactions with the used media (Hyman and Bagaasen, 1997; Noonan et al., 1993; Poulsen et al., 1996). Soil flushing, soil venting, and soil vapor extraction are the most traditional physico-chemical techniques. Soil flushing washes out the soil by combining groundwater extraction and infiltration of clean water. Chemicals can be added to the water used for the extraction. Soil flushing is suitable for cleaning zones with a permeable matrix and when contaminants are soluble into the water or do not stick too strongly to the soil matrix. Contaminants, which can be removed by this technique, are aromatics, chlo-

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rinated solvents, and some heavy metals. A disadvantage is the long duration required to clean and to attain a very low residual concentration. Soil venting consists of an injection of a forced air stream through the contaminated soil matrix: the pollutants, in this way, are stripped and carried out from the soil together with the air phase. However, the soil venting is only suitable for the removal of volatile contaminants such as hydrocarbons. With soil vapor extraction (SVE), the gas phase in a contaminated soil matrix is taken out under vacuum by one or more wells. Pressure gradients induce convective air flow throughout the porous soil matrix. As the contaminated gas is removed, clean air from the surface is drawn into the noncontaminated zones. Depending on their vapor pressure, organic volatile compounds are thus extracted by convective currents through the soil. SVE is a very effective technology for remediation of soils contaminated by many petroleum derivates, due to their highly volatile nature. Soil porosity promotes the air moving currents. SVE is even more effective when it is coupled to other remediation techniques, like soil venting and/or thermal treatment of the soil bulk. *Ex situ* physico-chemical treatments are performed as a solvent extraction. Solvent choice and setting of all the process parameters (contact time, mixing, temperature, and so on) are crucial (Hyman and Bagaasen, 1997; Tatàno, 1999).

Biological cleaning treatments are applicable to soils contaminated with degradable compounds. Microbiological techniques consist of the transformation of complex pollutants into harmless singular compounds by microorganism activity (Hyman and Bagaasen, 1997). There are many ways to employ a microbiological digestion (Tatàno, 1999). Land farming, composting, and bioreactor are the most diffused experiences for *ex situ* treatments and are especially applied on soil contaminated with gasoline or mineral oil. These techniques are based on the processes naturally occurring due to the presence of endogenous microorganisms. Parameters such as temperature, nutrients, pH and oxygen concentration may be helpful in improving the kinetic of the microbiological digestion. In particular, polluted soils are treated in bioreactor processes as active sludge installations for water treatments. *In situ* biodegradation involves techniques based on circulation of an air steam through the soil both under vacuum (via extraction of the air) and in pressure (via air injection) with pipes and wells connected to vacuum pump system or blowers, respectively. To enhance the kinetic of biodegradation, hot air may be insufflated. In this case, auxiliary equipments for water and nutrient sparging are adopted due to the drying phenomena taking place through the soil matrix during the air fluxing. In recent applications, radio frequency (RF) heating has been used to improve biological cleaning conditions by raising the soil temperature to such a level that the activity of the microorganism was at its highest (Janseen-Mommen and Jansen, 2001). Applications of biological treatments are, however, hindered by some significant disadvantages such as remarkably long duration of cleaning, difficulties of attaining very low residual concentration of the pollutant compound, and possible need of soil conveyance (*ex situ* treatments). Finally, in cold weather contaminated areas, the microbiological activity is too low to make bioremediation applicable.

Thermal treatments are performed by heating the contaminated soil matrix in many different ways. In particular, *in situ* treatments are possible using electrical energy, radio frequencies, and steam injections (Buettner and Daily, 1995; Price et al., 1997; Regan et al., 1995; Hyman and Bagaasen, 1997). Basic mechanisms are: desorption, vitrification, and incineration. Desorption and vitrification processes even typical for *in situ* applications are often employed to clean contaminated soil in off-site plants. Evaporation, degradation, and immobilization of pollutants are performed by raising the soil temperature to 500–1200°C. Exhaust, once chemically inert, can be used in construction applications or replanted in their originating sites. Incineration may require very high temperatures, typically up to 2,000°C, and, thus, becomes an expensive treatment (Hyman and Bagaasen, 1997; Tatàno, 1999). However, it is often the only way to immobilize some hazardous pollutants.

VOCs removal

Semi-volatile and volatile organic compounds (SVOC and VOC, respectively), are classified in the category above due to their chemical and physical characteristics. They have been the subject of a significant scientific interest from researchers worldwide, as they actually are among the major pollutant substances everywhere.

Remediation of VOCs polluted soils is mostly performed by SVE (Hyman and Bagaasen, 1997; Poulsen et al., 1996; Noonan et al., 1993). With this technique, soil matrix can be treated *in situ* for the removal of hydrocarbons, and the process is based on physical equilibria (evaporation), as well as on mass-transfer phenomena (convective currents). As reported above, SVE treatments show a fairly good efficiency of remediation. However, times required are in the order of months. The concept of heating soil to facilitate desorption and volatilization processes is not new (see thermal treatments), and is applied now in ancillary processes to be added to SVE. Indeed, both electrical heating and electromagnetic radiation were used in the 1970s to recover bitumen from tar sand deposits. In this way, bitumen viscosity was lowered, resulting in easier recovery operations. Further heating treatments were applied in the 1980s and 1990s to the remediation of airfield soils contaminated by petroleum products (Kang and Oulman, 1996; Kawala and Atamanczuk, 1998; Lee et al., 1998; Jones et al., 2002).

Many auxiliary processes have been proposed to both increase efficiency and decrease times for VOCs removal. They are based on the heating of the soil matrix to give place to two kinds of remediation processes: volatilization of contaminants (alternatively, hot breakdown of complex molecules and then volatilization) or pollutant extraction via steam distillation operations.

Noonan et al. (1993) have reported results of air sparging and steam injection techniques to enhance the performance of SVE applied on hydrocarbons polluted soil. Air sparging (or air injection) promotes remediation processes because of the influence on the oxygenation of the depth layers and on the increases of convective currents inside the soil matrix. Steam injections are especially effective with SVOC, due to their better carrier-phase properties such as density and thermal capacity. Buettner and colleagues (Buettner and Daily, 1995) studied the SVE/electrical heating combination. They performed experiments in a trichloroethylene polluted soil using Joule heating applied with underground resistances powered by high voltage electrodes. Radio frequency heating (RF), as ancillary process to be added to SVE, has been proposed by Price et al. (1997) to clean by *in situ* operations a gasoline polluted zone of Minnesota. RF energy was delivered by an antenna applicator (27.12 MHz frequency and 5 KW power) located in an underground tube between the extraction wells of the SVE equipment. Regan's research group (Regan et al., 1995) performed lab-scale experiments on beds of soil-sand polluted by chlorinated hydrocarbons using RF energy, similarly to Price et al.

The combined techniques above actually improve the SVE treatment and are relatively expensive since they suffer from the need to build equipment on-site, such as industrial plants to perform injections or vacuum extractions, and electrical high voltage circuits inside the soil. Therefore, the idea of an endogenous generation of heat or water vapor inside the soil matrix by application of an electromagnetic field appeared to be enticing. Abramovitch and colleagues (Abramovitch et al., 1998, 1999 a,b) applied the dielectric heating to remedy polychlorinated aromatics polluted soil. They performed the pollutants decomposition by microwave treatments using selected "thermal adsorbents" such as metallic powders and graphite. George et al. (1992) studied the aromatic hydrocarbons desorption processes from sand and soil matrix applying microwave heating enhanced by carbon particles. Windgasse and Dauerman (1992) focused their work on the endogenous generation of water vapor to promote the water-stripping of VOC pollutants from soil. The authors studied the feasibility of a new technique to develop the removal of contaminants in the presence of soil moisture by an *in situ* steam distillation process. The relevance of this new kind of treatment consists in that it is a nonintrusive technique associated to the absence of thermal stresses. Indeed, the electromagnetic energy penetrates in the soil matrix layer by layer without any invasive antenna. The soil humidity fixes the upper remediation temperature to 100°C, that is, the boiling temperature of the water that, once vaporized, catches the contaminants and removes them out of the soil.

Kawala and Atamanczuk (1998) developed further studies on the steam distillation process induced by radio frequencies heating by pointing out the role of polar compounds, such as water, on the remediation treatment. They used beds of soil-sand polluted by chlorinated hydrocarbons, and a pre-pilot apparatus similar to the ones used with the SVE technique.

Basic concepts of microwave heating

All the processes performed by microwaves/RF heating outlined that microwave heating may offer, in comparison to more conventional steam injection or electrical heating, advantages such as shortened treatment times, selective heating, reduced environmental impact because of reduced soil manipulation, accurate control of the process parameters, and, consequently, increased safety (Thostenson and Chou, 1999; Jones et al., 2002).

All above directly come by the peculiar characteristics of microwave heating. Microwaves are electromagnetic radiation with a wavelength ranging from 1 mm to 1 m in free space with a frequency between 300 GHz to 300 MHz, respectively. The microwaves frequency more often used is 2.45 GHz, which is adopted in both industrial and scientific applications. In the microwave process, heat is internally generated within the material, rather than originating from external sources. The heating is very fast as the material is heated by energy conversion rather than by energy transfer, as, in contrast, occurs in conventional techniques. The ability of a material to absorb energy is related to its permittivity. This property is reported in the form of a complex number and is usually indicated with the Greek symbol ϵ. The real part ϵ' is known as dielectric constant and it is used as a relative measure of the microwave energy density in a material. The imaginary part ϵ'' is termed as a loss factor and accounts for the loss energy dissipative mechanisms. Knowledge of the dielectric properties of materials to be processed via microwave is essential to the proper set up of a working protocol. Generally speaking, the dielectric properties of a material are related to frequency, temperature, moisture content, density, and material geometry (Gardiol, 1984; Metaxas and Meredith, 1988). It is worth noting that the moisture content of the material may be relevant in microwave processes, with its role depending on whether molecules of water are either bond or free of moving (Kraszewski, 1996; Metaxas and Meredith, 1988).

MISD process

In this work, decontamination of volatile organic compounds is performed via microwave heating. In particular, the feasibility is investigated of the steam distillation process induced by dielectric heating to remedy soil carrots contaminated with naphthalene. The decontamination process adopted is named microwave induced steam distillation (MISD), to emphasize the role of the microwave heating, and can be depicted as follows (Barba, 2001). A real system, when irradiated with microwaves, dissipates the energy associated to radiation, giving place to a temperature increase based on its dielectric properties. The temperature profile follows the exponential decay of the electromagnetic field, whose penetration depth is defined as the distance when the field intensity decreases to 1/e of its initial value. If microwaves are irradiating a soil-water-VOC system, then the first layers of soil show a significant temperature increase, which reasonably results in a loss of water in the form of vapor, as this is the major dissipating component of the system. This substantially occurs in a thickness of soil strictly related to the specific penetration depth of the microwave field, once again according to the exponential profile of the field intensity. Since the dielectric properties of the soil matrix change layer by layer with physical and chemical characteristic changes of the soil due to the progress of microwave treatment, the superior soil layers, now dried, become transparent to microwaves so that the electromagnetic field moves deeper inside in a sort of boundary layer process, then, everything reproduces.

In this work, attention is focused on mass- and heat-transfer phenomena through the soil undergoing the treatment, as the remediation is associated to both vapor and VOCs leaving the soil as an effect of heat generation and transport. The work aims at formulating the base statements for modeling the transport phenomena in the irradiated soil, towards its practical realization.

Experimental Studies

As from considerations above, key parameters of the MISD process appear to be soil characteristics, the microwaves penetration depth, and the moisture content of the soil. Nevertheless, the fate of the water plays a major role since, as shown in preliminary tests (Acierno et al., 1998), pollutant removal is as high as 95% in a few minutes of exposure to microwaves, and strictly follows the water vapor migration. Experiments have thus been mainly devoted to study the behavior of the water in the soil during the microwave irradiation, and to elucidate the relative role of the other parameters.

Three different kinds of experiments have been, thus, set up and performed, as described in the following:

- Soil dielectric characteristics have been directly measured by a network analyzer;
- Effect of water content on the remediation process has been studied by measuring temperature and moisture profiles in soil samples undergoing the microwaves treatment; and
- Migration of the pollutant-steam phase through the soil has been observed by decontaminations runs.

Heat- and mass-transfer phenomena have been studied by designing a soil sample holder that was representative of a semi-infinite portion of real contaminated soil, which extends on a large surface, which is the depth of the direction to be explored for remediation purposes. The soil selected for the experiments had to be available in a large quantity at constant characteristics. In addition, contaminant concentration in the soil at the beginning had to be always the same. Finally, the experiments had to be easily feasible, heading to possible future *in situ* applications.

Materials

Naphthalene was selected as model soil contaminant. Naphthalene is solid (at room temperature) and insoluble in water so methanol was used as a solvent to disperse naphthalene in the soil matrix. A commercial (gardening) soil (particles Sauter mean diameter 300 μm) was used as a model porous soil due to its large availability at constant composition.

Apparatuses

A 2,450 MHz, 800 W maximum power, closed multimode microwave oven was used to treat the previously contaminated soil samples with given quantities of naphthalene at different moisture contents. To reduce the effect of a hot spot (a typical problem in microwave multimode cavity is the nonuniformity of the field distribution, thus, the nonuniformity of the heating process), an oven equipped with a turntable that rotates during a heating process has been chosen. By this way, the loads (soil carrots) achieved a homogenous heating during the runs passing through areas of high and low electromagnetic field intensity.

Microwave dielectric properties of the samples were nondestructively measured at 2,450 MHz using an HP 851907B vector network analyzer with a dielectric probe meter HP 85070B, under the various operating conditions. Some Soxhlet equipment was used to extract the contaminant from the soil for the purpose of analysis by using a methanol-naphthalene solution. Analyses were performed by a HP 5890 gas-chromatograph.

The sample holder was made of steel with a cylindrical shape of 10 cm in diameter and 12 cm in length. It was thermally insulated and put in a vertical position in the microwave oven to simulate a real portion of soil. Horizontal marks every 1 cm were put on the sample holder walls to help in the removing of a given size (Figure 1).

Methodologies

All the experiments are performed on samples prepared by sieving, drying under a vacuum at a low temperature, and eventually humidifying given quantities of soil. Following the above indications, soil samples were purposely prepared at different moisture content. Water is added to the dry soil to obtain different moisture levels (from dry (0.3 $kg_W\ kg_S^{-1}$) to very humid (1.5 $kg_W\ kg_S^{-1}$) soil matrix). By this way, water content is in the range typical for real soils.

Permittivity tests were performed on small samples of soil placed under the probe of the vector network analyzer. Each sample was prepared adding given amounts of water to dry soil, and heated to investigate the dependence of the loss factor from both humidity level and temperature.

Temperature and water content profiles of the soil during microwave treatment were determined to account for any change in the soil due to the power delivered by the microwaves. Runs were performed on soil-carrots in a semi-continuous way. After a given period of treatment, the run was stopped and temperature was measured using six thermocouples simultaneously. The sample was eventually put in the oven for a new set of temperature measurements, or removed layer by layer to the water content analyses. Mass samples used ranged from 0.250 to 0.500 kg, depending on the quantity of water added. Exposure time to microwave,

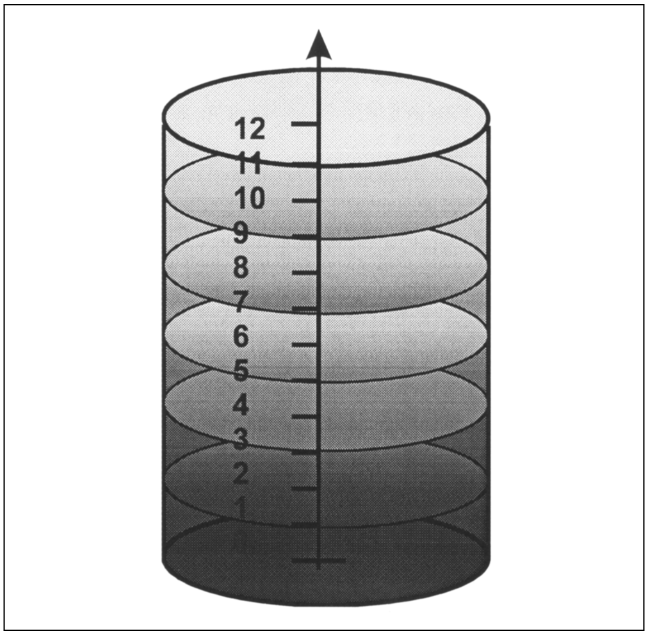


Figure 1. Horizontal layers of the soil carrot scheme.

power delivered, and water content of soil samples were changed during the runs.

Decontamination effect of the microwave treatment was evaluated by measuring the residual naphthalene in the soil by a 2 h Soxhlet extraction with methanol followed by chromatographic analyses of the solution.

Results and Discussion

Permittivity analysis

Changes of the loss values as a function of humidity at different temperatures are reported in Figure 2. As it is shown, dry soil is a weak microwave absorber, whereas soil-water mixtures have significant loss factor values after a critical moisture content. This point marks the transition from bond to free water in the soil matrix and, thus, the different ability of water to absorb the microwave energy. When temperature increases, the dielectric constant decreases according to the temperature dependence of the water (Figure 3) and to the relevant role that water has in the soil matrix permittivity.

The results above indicate that as soil becomes both hotter and dryer, microwaves pass more and more easily through the soil layers.

It has to be noted that the water loss factor values do not change above 100°C (Figure 3), that is, near to the steam distillation point.

Heat and mass transfer

Heat and mass transfer are studied in soil carrots put in the sample holder described above. In the following, the only axial coordinate has been explored since preliminary tests showed the absence of radial gradients for each of the investigated parameters.

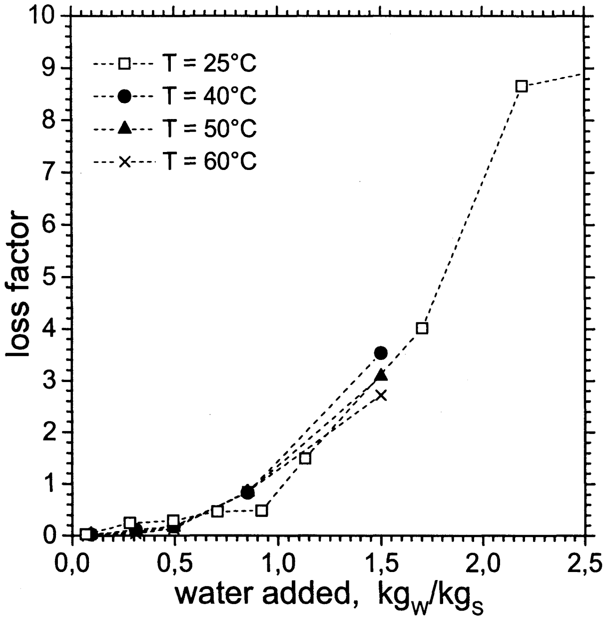


Figure 2. Loss factor values as a function of humidity measured, at different temperatures, in soil-water mixtures.

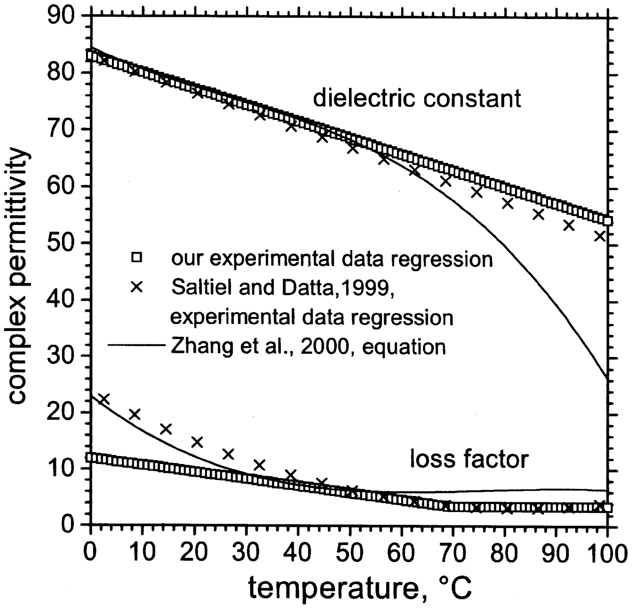


Figure 3. Water complex permittivity as a function of temperature at 2.45 GHz.

Temperature and humidity profiles represented, layer by layer, the steps of the microwave dissipation. All the measurements, that is, temperature and residual moistures, are performed under various operating conditions at different exposure times and for given soil moisture (see labels in figures). The power delivered is always 800 W. Results are given as a function of the distance from the sample holder bottom (Figure 1).

Temperature profiles are shown in Figure 4. Temperature increase in the soil is related to the electromagnetic field decrease with the soil depth, which depends in turn on changes of the dielectric loss values. As a matter of fact, samples with a low initial humidity (Figure 4a) show a microwave penetration depth in the order of 10–12 centimeters. Thus, microwaves penetrate through the whole length of the sample holder. Consequently, temperature rapidly increases up to the steam distillation point and eventually remains unchanged. Penetration depths are the lower as the soil carrot is more humid. For short exposure times, that is, 1 min, penetration depths are about 3–5 cm (Figures 4b, 4c, 4d, and 4e). All this emphasizes the sigmoid-like shape of temperature profiles. When the microwave treatment goes on, the temperature profiles move unchanged in shape, as is shown for 2 and 3 min of exposure to microwaves. In these carrots, the time is consequently longer for the microwaves to reach the bottom of the sample holder.

A cross-plot of temperature profiles measured after 3 min of microwave heating is reported in Figure 4f. It outlines the different ability of the soil layers to dissipate microwave energy, depending on their moisture content, and the temperature plateau at the water vaporization point. The profiles move in the soil with unchanged shape, due to the law of decay of the electromagnetic field. Once the water vaporization point is reached, the temperature does not increase further due to the water liquid-vapor transaction phase. Note that, since the steam distillation temperature is the maximum

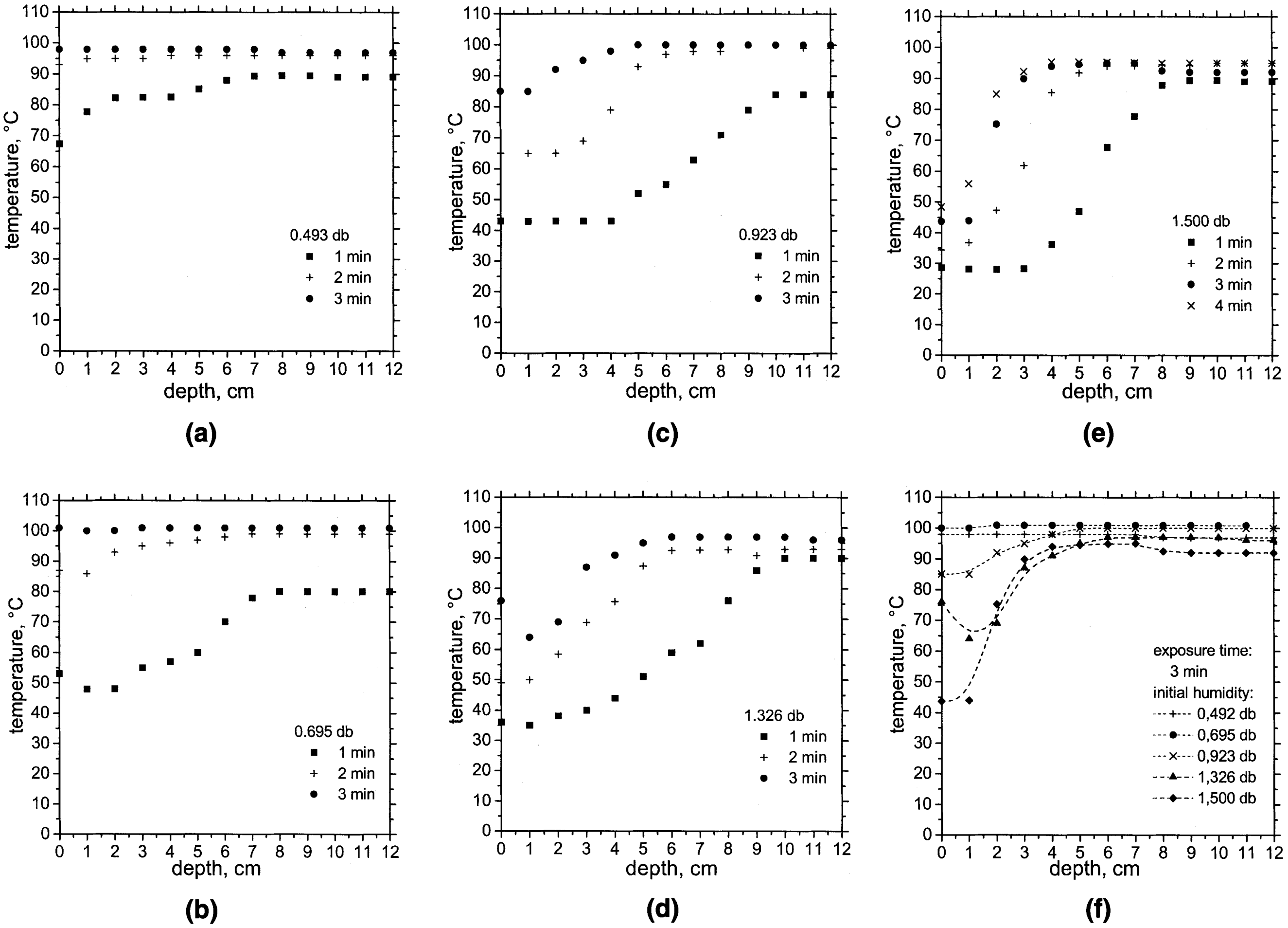


Figure 4. Temperature profiles in soil carrots as a function of depth for different initial moisture content and exposure time (humidity is indicated on dry basis (db)).

experienced by the soil during thermal stresses, it does not damage the organic composition of the soil matrix. Thus, the use of the decontaminated soil for agricultural purposes is not precluded. As a matter of fact, even thermal treatments which heat the soil matrix up to about 500°C do not irreversibly destroy organic and mineral structures, as, on the contrary, occurs when higher temperatures are achieved. Above 900°C, vitrification processes may occur (Tatàno, 1999).

The results show that microwave heating is very fast: a soil can reach the crucial point for the stripping process, that is, 100°C, in less than 5 min. On the contrary, times for the relaxation process, that is, the soil cooling down process, are two orders of magnitude larger. Indeed, previous results showed that about 3 h are necessary to bring the soil temperature from 100°C down to room temperature (Acierno et al., 1999). The cooling phase is thus slow enough to let evaporation occur for a relatively long time. In Figure 5 the different rates of heating and cooling processes can be seen. Runs were performed as follows. After one min of microwave treatment (curve a), the oven was turned off. Temperature profile was measured after two more min (curve b): in the absence of microwaves, the temperature slowly decreased in all the soil layers. On the other hand, temperature profile was measured after the same first heating step, that is, one min of exposure time. With two min of further microwave treatment (curve c), the temperatures rapidly increased and the steam distillation point was achieved for about half of the soil sample.

Humidity profiles are shown in Figure 6. For short exposure times, temperature increases are moderate, and only a little amount of water evaporates out of the sample. On the contrary, for longer exposure times, considerable amounts of water evaporate because of the higher temperatures reached. A drying process occurs layer by layer, from the surface to the bottom, according to changes of the dielectric loss values recorded in the permittivity measurements. Indeed, when the water is progressively taken out from the superficial soil layers, the microwaves passage through the soil carrot is easier since the dry soil is a weak absorber. It has also to be noted that the vapor, which moves from the bottom to the surface of the soil carrots, does not condense due to the higher temperature on the superior layers (about 100°C, which is the boiling point of water).

Decontamination runs

Decontamination profiles obtained under different exposure times to microwave are given in Figure 7. All the polluted samples have an initial contaminant concentration of

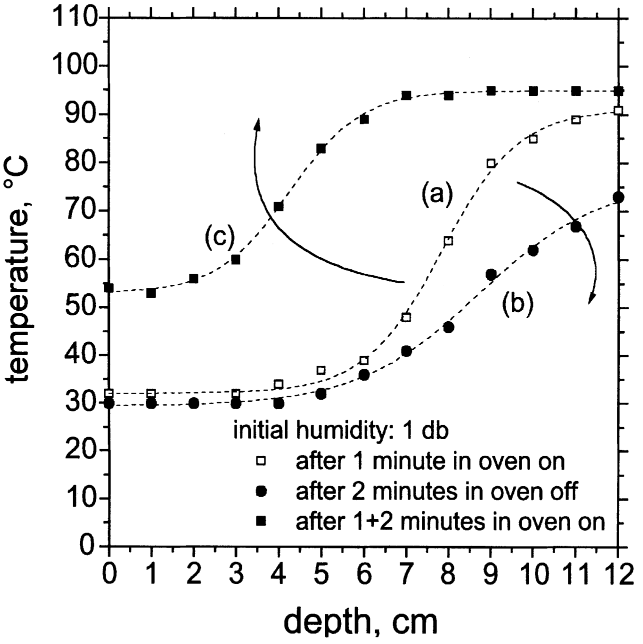


Figure 5. Thermal profiles during heating and cooling processes.

2,000 ppm and a humidity of 0.82 on dry basis (db), and are exposed to microwaves for times ranging from 3 to 10 min. Power supply is 800 W. Results are reported in terms of percentage of residual naphthalene as a function of distance from the sample holder bottom.

For irradiation times from three to five min, naphthalene is significantly stripped out of the first two layers. Deeper layers still contain a considerable amount of contaminant, as microwaves penetrate only a few centimeters depth. This is in accordance with the heat and mass transport observed in the samples at the same conditions of water content and time of exposure (Figure 4 and Figure 6). For longer times, that is, 7–10 min, naphthalene is progressively taken out of the polluted matrix by the induced steam distillation, so that only a portion of it remains into the whole soil sample. Performance enhancements of soil decontamination treatments are possible by increasing the initial moisture level and exposure time, as reported by Acierno et al. (1998). Note that removal efficiencies may be based on the residual concentration imposed for each contaminant, by the environmental requirements of the given country.

Decontamination profiles confirm the phenomenology described above (Acierno et al., 2000b). The first layers of the contaminated soil matrix show a significant temperature increase, which in turn results in a loss of water in the form of contaminated vapor (pollutants and stripping phase). Thus, the dielectric properties of the irradiated system change layer by layer basically with the changes of water content of soil due to the progress of the microwave treatment. This in turn depends on the time of exposure. When the superior soil layers are dried, these become transparent to microwaves so that the remediation process moves deeper inside, and everything reproduces. In this way, good performances of the MISD process down to 10 cm depth are obtained in 10 min of superficial microwaves radiation heating.

Modeling

Phenomenology of the MISD process investigated above shows that the mass and heat transfer are subordinated to the loss properties of the irradiated matter and that all the physical properties are strongly interlaced. The following model reports the mathematical description of heat and mass evolution during microwaves exposure in soil-water systems. Naphthalene is disregarded in this phase, since attention is focused on water, which is the strongest microwave absorber. Actually, soil and contaminant have a very low loss factor.

The MISD process has been modeled with coupled monodimensional transient equations of energy (Eq. 1) and mass (Eq. 2) balance; the generation term takes into account the interactions between the electromagnetic field and matter and, finally, the electromagnetic relationships are related to plane waves propagation (Acierno et al., 2000b). Note that only the axial direction has been considered for the model, since radial temperature and moisture gradients are negligible, as also evidenced in the Experimental Studies section.

The model does not take into account percolation and diffusive phenomena in the soil matrix. Actually, the dynamics of both microwaves soil heating, and vapor-phase formation and convective related fluxes, is much faster than any diffusive phenomenon, whereas percolation is hindered by the porous nature of the solid itself.

The model equations are

$$(1-p)\cdot\left[K_{TM}(T,X)\frac{\partial^2 T}{\partial z^2}\right]+\dot{Q}(T,X)-r_v(T)\cdot\lambda_w(T)$$

$$=(1-p)\cdot\rho_M(T,X)c_{pM}(T,X)\frac{\partial T}{\partial t} \quad (1)$$

$$(1-p)\cdot\rho_S\frac{\partial X}{\partial t}=-r_v(T) \quad (2)$$

The initial and boundary conditions are

$$\text{I.C.} \quad @t=0, \quad \forall z>0, \quad T(0,z)=T_0 \quad (3)$$

$$\text{I.C.} \quad @t=0, \quad \forall z>0, \quad X(0,z)=X_0 \quad (4)$$

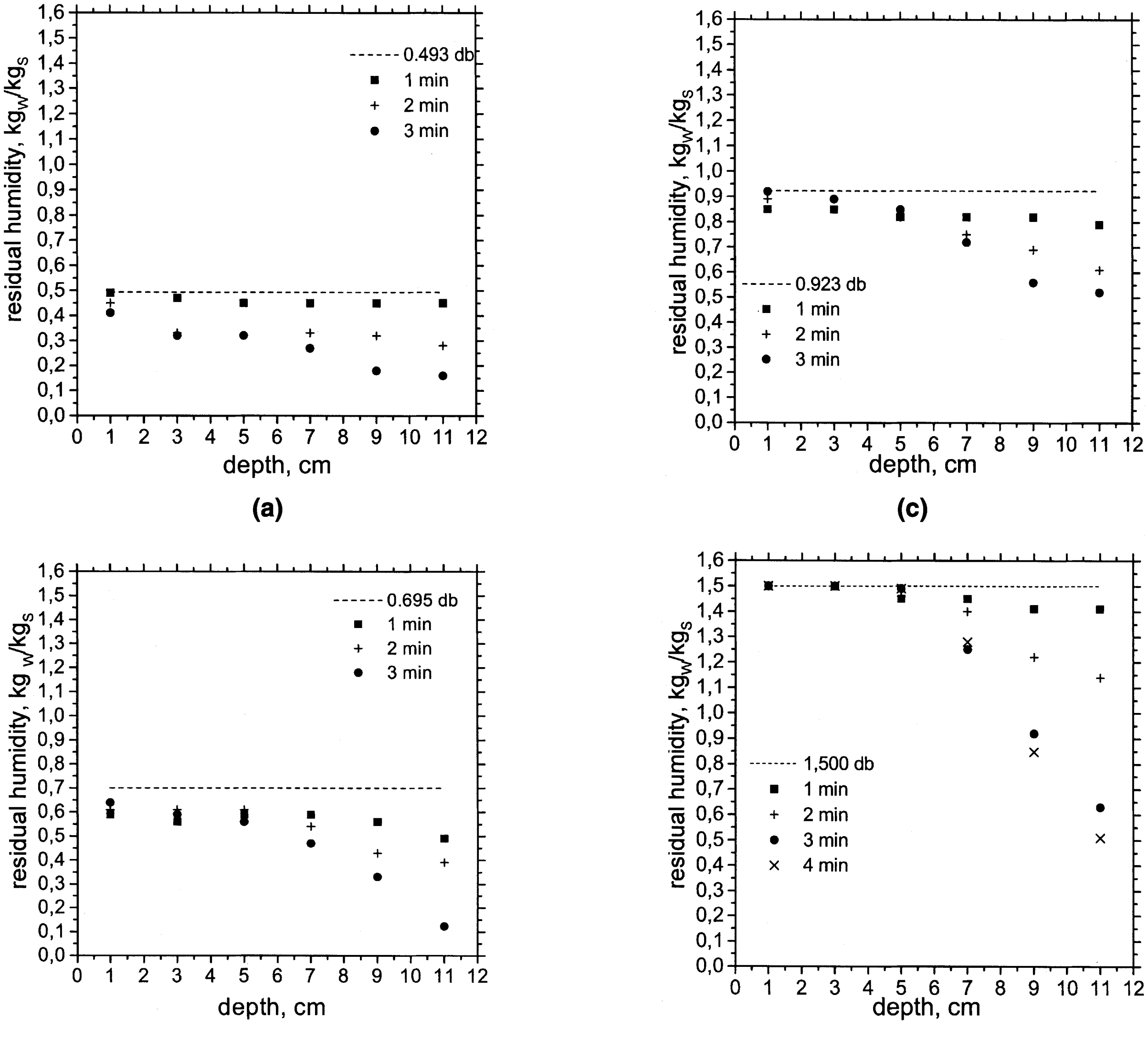
$$\text{B.C. 1} \quad @z=0, \quad \forall t>0, \quad K_{TM}\left.\frac{\partial T}{\partial z}\right|_{z=0}=-h\left[T(t,0)-T_a\right] \quad (5)$$

$$\text{B.C. 2} \quad @z=L, \quad \forall t>0, \quad \left.\frac{\partial T}{\partial z}\right|_{z=L}=0 \quad (6)$$

The energy generation term takes into account the interlacing between dielectric properties, temperature, and water content of the treated systems. The generation term $\dot{Q}$ can be expressed as follows

$$\dot{Q}(T,X)=\frac{1}{2}\omega\cdot\epsilon_0\cdot\epsilon''(T,X)\cdot E^2(T,X) \quad (7)$$

$\dot{Q}$ strongly depends on both power of the radioactive source and permittivity of the irradiated system.



(a)

(c)

(b)

(d)

Figure 6. Residual humidity profiles in soil carrots as a function of the depth for different initial moisture content and exposure time (humidity is indicated on dry basis (db)).

The soil complex permittivity has been previously modeled by Acierno et al. (2000a) as a function of the water content of the soil and its availability to participate to the dissipation process, and of the temperature (Figure 8). This has been described in the model through a water activity function $f(X)$, which in turn depends on the pore-size distribution of the soil. Thus

$$\epsilon_M(X,T) = \epsilon'(X,T) - i\epsilon''(X,T) = \frac{1/\rho_{SS}}{1/\rho_S + f(X)}\epsilon_S(T) + \frac{f(X)}{1/\rho_S + f(X)}\epsilon_W(T) \quad (8)$$

where f is the water activity function

$$f(X) = \int_0^X g(r(X)) \cdot dX \quad (9)$$

In Eq. 9 $g(r(X))$ is the connection between the radius of a pore and the activity of the water contained in it.

To evaluate the traveling electrical field intensity in Eq. 7, one must consider that a number of problems in microwave engineering can be regarded in terms of a planes electromagnetic waves incident on semi-infinite media. The solution of Maxwell equations in this case leads to

$$E(T,X) = E_0(T,X) \cdot \exp(-\alpha(X,T) \cdot z) \quad (10)$$

where the coefficient α, for a low loss medium (that is, $\epsilon''/\epsilon' < 1$), can be written as (Metaxas and Meredith, 1988)

$$\alpha(T,X) = \frac{2\pi}{\lambda}\frac{\epsilon''(T,X)}{\sqrt{\epsilon'(T,X)}} \quad (11)$$

In Eq. 11, λ is the wavelength of the electromagnetic field at 2,450 MHz. The coefficient α gives the attenuation of the

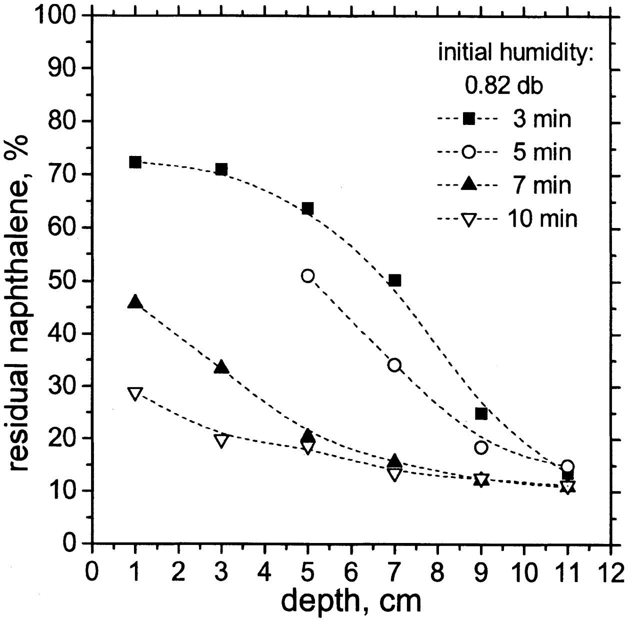


Figure 7. Decontamination profiles of residual naphthalene as a function of depth at different exposure time (initial humidity: 0.82 $kg_w\ kg_S^{-1}$).

electrical field. Its reciprocal, the penetration depth, is usually employed, and is defined as the distance from the surface of the material at which the power drops to e^{-1} from its value at the surface.

It is well known that the heat transfer and electromagnetic field are strongly coupled in microwave heating. Thus, to achieve the desired power dissipation, different values of the electrical field are required for different dielectric media. As a consequence, for a given heating time unit, different values of the incident electric field (E_0) are induced during the heating of different materials on the basis of their loss factors. A relationship between the incident electric field and loss factor of the material has been obtained for the oven used in this work by calorimetric measurements on the small amount of well characterized dielectrics.

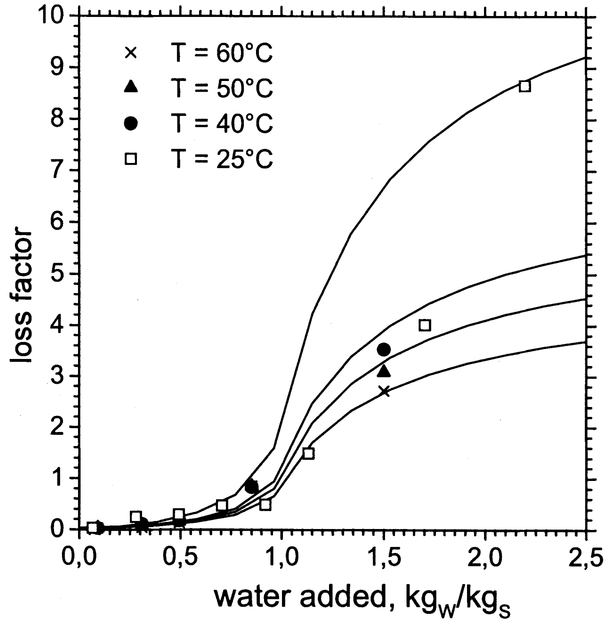
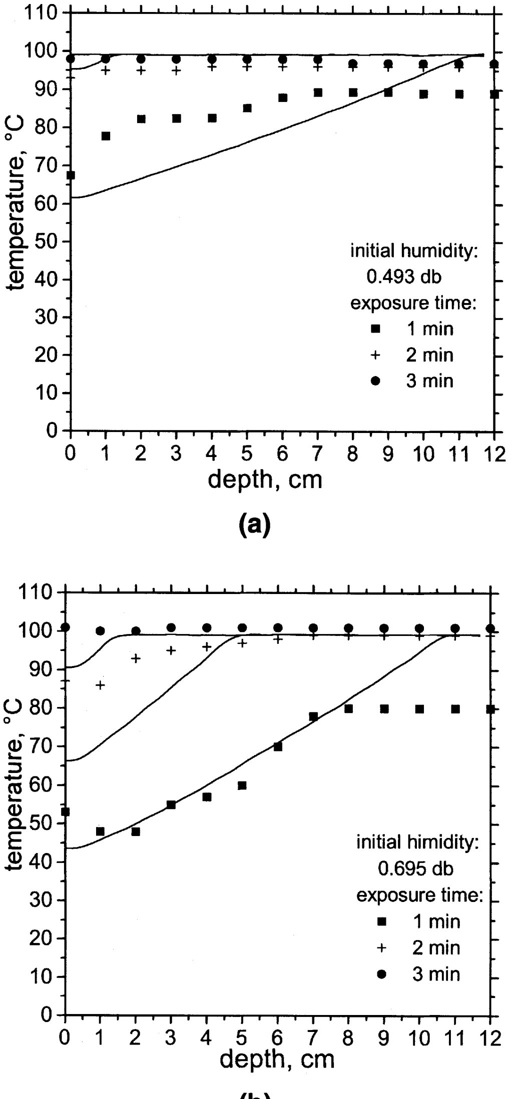


Figure 8. Measured loss factor values and model curves as a function of water content at different temperatures at 2.45 GHz.



(a)

(b)

Figure 9. Model predictions of temperature profiles as a function of the depth for different initial moisture content and exposure time.

Humidity is indicated on dry basis (db).

The r_v term in Eqs. 1 and 2 is the rate of vaporization, that is, the vapor flux that leaves the soil particles surface and goes into the steam/air phase. Its values are related to the different pressure between the liquid water vapor pressure and the partial pressure of the gas phase. This pressure gradient is, at the end, a function of the temperature.

In the model, the r_v term is calculated by modifying a relationship available from studies on drying operation of porous

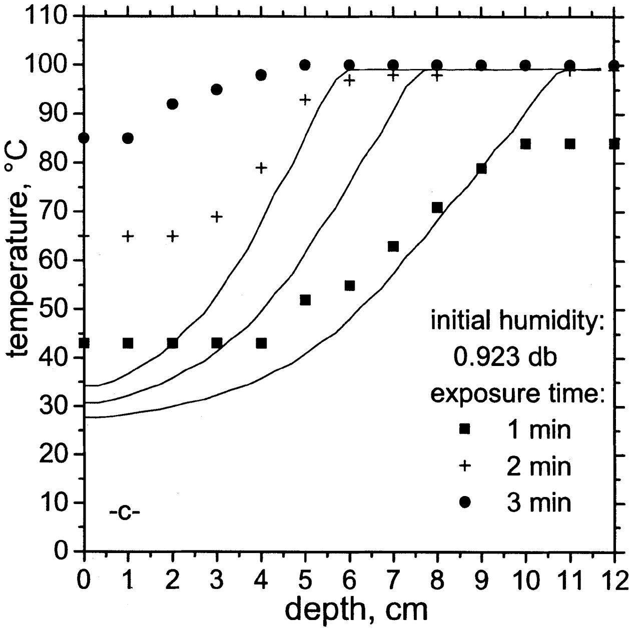


Figure 10. Model predictions of temperature profiles as a function of the depth for different initial moisture content and exposure time.

Humidity is indicated on dry basis (db).

media and granular solids (Coulson et al., 1978; Foust et al., 1992)

$$r_v(T) = \frac{k_c \cdot a}{RT} \cdot 0.018 \cdot P_S(T) \tag{12}$$

where k_c is the mass-transfer coefficient, a is the specific area of the transfer phenomenon, and 0.018 is the molar weight of the water (kg/mol).

The proposed model does not take in account the VOC mass balance. However, correlation can be stated between vapor stream generated and naphthalene recovery. Stripping efficiencies are indeed related to the generation of steam currents, which is the focus of the Modeling section.

The partial differential equations (Eqs. 1 and 2) with their initial conditions (Eqs. 3 and 4) and boundary conditions (Eqs. 5 and 6) are solved by the finite difference method known as the Crank-Nicolson scheme.

Model results

Predicted and experimentally determined temperatures and residual humidities are compared in Figures 9–10 and Figures 12–14.

In the figures, modeled temperature profiles are reported as a function of depth and compared to the experimental results obtained with a 12 cm deep soil sample. As above hypothesized, the temperature profile moves deeper and deeper without significantly changing its shape (that means without changing the kind of phenomenology), confirming the idea of a boundary moving problem.

Model and experimental results reported in Figures 9a and 9b well agree.

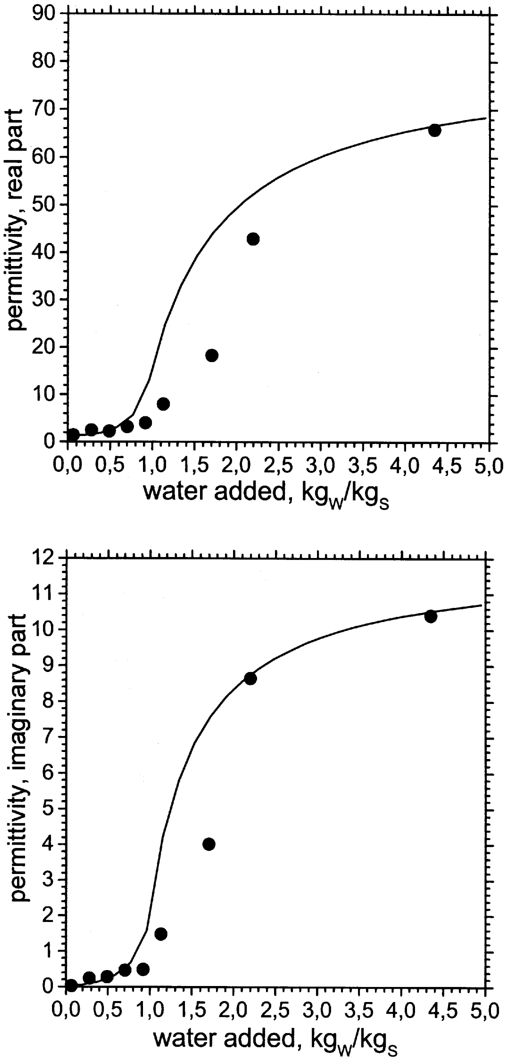


Figure 11. Real and imaginary part of the complex permittivity as a function of the water content (model curve: -; experimental ●) @ 2.45 GHz and 25°C.

However, when the soil humidity reaches the critical value previously outlined, where the water is no more bonded to the soil, model curves do not match with experimental data (Figure 10).

It has to be reminded that, in the model, soil permittivity is theoretically predicted, as shown in Figures 8 and 11, with satisfying results but for a certain soil humidity range centered at the critical value, that is, 1–2.2 db. The range is the smaller, as the temperatures are higher. It is noteworthy that the disagreement between predicted and measured temperature profiles occurs in the same humidity range.

As a consequence of the overestimation of the theoretical permittivity, penetration depth is underestimated and, thus, energy dissipation is predicted to occur in a lesser deep layer than the experimental one. The deviation of the theoretical permittivity from the measured value in the critical humidity range pointed out above has been accounted for in the model calculations by a corrective factor (Figure 12).

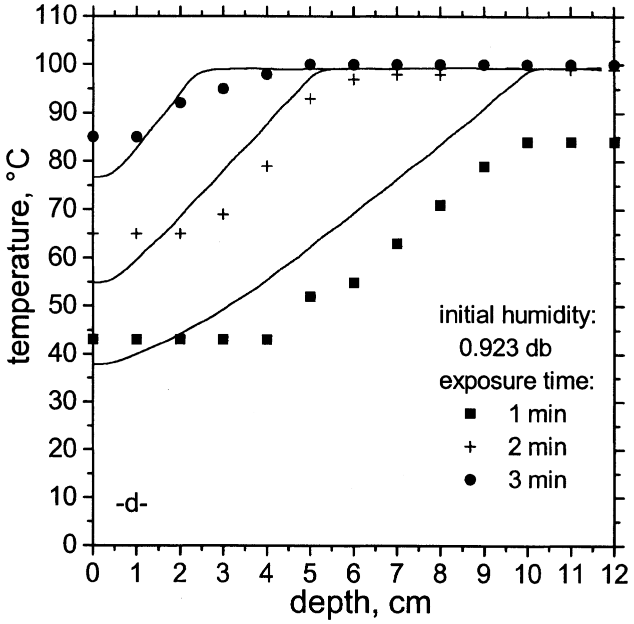


Figure 12. Model predictions of temperature profiles as a function of the depth for different initial moisture content and exposure time.

Humidity is indicated on dry basis (db).

The value of the corrective factor has been optimized, resulting in the same for all the runs in the critical humidity range (Figures 13a and Figure 13b).

Modeled residual humidity profiles, obtained by coupling mass and heat transfer, show the same disagreement close to the moisture transition zone. As reported above for the temperature profiles, a good agreement between experimental data and calculated profiles may be obtained by the same corrective factor.

Conclusions

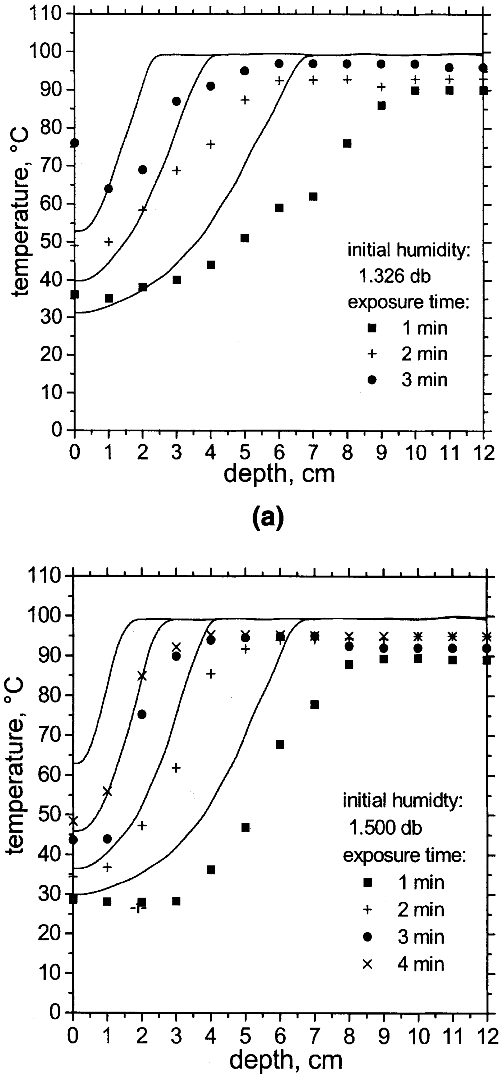
The propagation of the electromagnetic waves in a polluted soil undergoing remediation, and the related heat and mass transfer, have been analyzed and modeled. The critical parameters of the process have been identified.

The microwaves treatment of soil carrots in a closed applicator shows that a superficial irradiation induces a deep heating. The progress of the heating front is allowed by the simultaneous progressive drying of soil, which in turn modifies the dielectric properties of the soil itself. The generated vapor flux moves towards the surface and permits a stripping process start, which takes the pollutant substances out of the soil matrix.

A predictive model has been formulated which puts together evolution of temperature, humidity, and permittivity of the soil during the microwave treatment. Model calculations satisfyingly agree with the experimental results.

The peculiarity of the microwave treatment, which is an *in situ*, nonintrusive operation, coupled to the absence of thermal gradients and to the mild temperature of the process, outlines the low impact of this new methodology. The soil in this way remedied can be even used for agricultural purposes.

Temperature and residual humidity profiles show that it is possible to reach the steam distillation point and to generate a vapor stream in a short time by the nonconventional heat-transfer phenomenon. *In situ* traditional heating operations, such as electrical energy or steam injections (see Introduction section), require a longer process time and/or intrusive equipments due to the physical properties of the soil-water systems. Indeed, conductive and convective heating phenomena are discouraged because of the low thermal coefficient, low electrical conductibility, and the complex operations to prevent short circuit or high-pressure drops of injected vapor fluxes in porous media such as soils. As a consequence, even if cost and power requirement estimations are difficult to make at the moment, microwave heating can be seen as an



(a)

(b)

Figure 13. Model predictions of temperature profiles as a function of the depth for different initial moisture content and exposure time.

Humidity is indicated on dry basis (db).

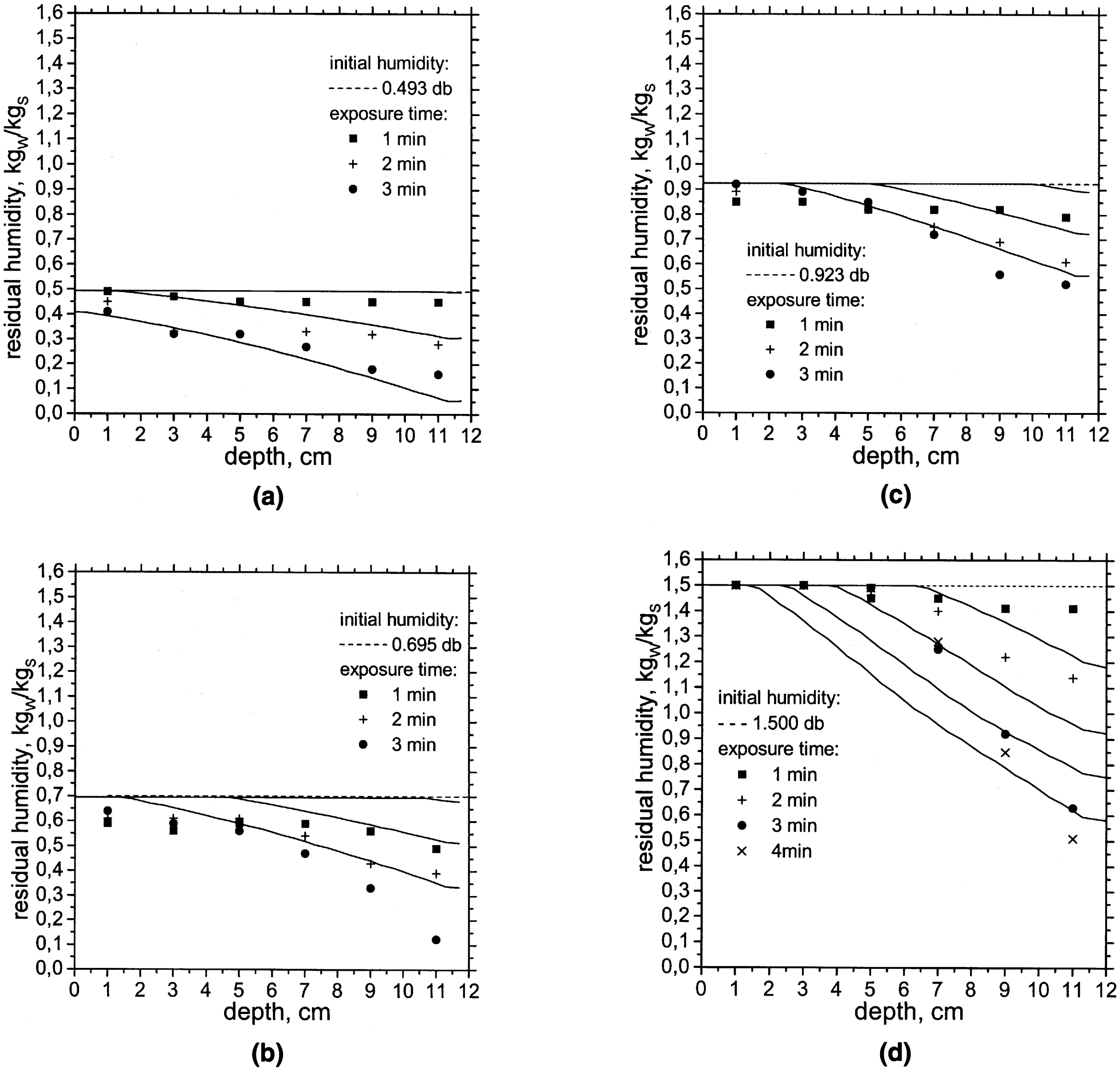


Figure 14. Model predictions of humidity profiles as a function of the depth for different initial moisture content and exposure time.

Humidity is indicated on dry basis (db).

innovative cost and time-saving operation. This, added to the effectiveness of the process, strongly encourages the design and the development of a dedicated applicator for *in situ* operations.

Notation

a = specific area, m^2/m^3,
c_p = specific heat, J kg^{-1} K^{-1}
db = dry basis (see X)
E = electromagnetic field intensity, V m^{-1}
E_0 = incident electromagnetic field intensity, V m^{-1}
k_c = mass-transfer coefficient, m s^{-1}
K_T = thermal conductivity, J m^{-1} s^{-1} K^{-1}
h = convective heat-transfer coefficient, J m^{-2}s^{-1}
L = maximum depth, m
p = porosity
Ps = water partial pressure, Pa
Q = power density, J m^{-3}s^{-1}
r_v = water evaporation rate, kg$_W$ m^{-3}s^{-1}
R = gas constant, J/mole K
t = time, s
T = temperature, K
X = moisture content, kg$_{H2O}$ kg$_{solid}^{-1}$
z = space coordinate, m

Greek letters

α = attenuation coefficient of the electromagnetic field, m^{-1}
ϵ_0 = vacuum permittivity, F m^{-1}
ϵ' = dielectric constant
ϵ'' = loss factor
λ = wavelength, m; latent heat of evaporation, J kg^{-1}
ρ = soil density, water density, kg m^{-3}
ω = angular frequency

Subscripts and superscripts

W = water
M = soil-water mixing
S = dry soil

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