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GROUNDWATER POLLUTION IN POROUS MEDIA BY FLUIDS IMMISCIBLE WITH WATER

F. SCHWILLE
Federal Institute of Hydrology, Koblenz (F.R.G.)

ABSTRACT

The principle of migration of fluids immiscible with water in porous rocks is demonstrated by means of mineral oil products and chlorohydrocarbons.

INTRODUCTION

The migration of fluids underground depends on the type and composition of the rock formation as well as on the type and composition of the fluid. In groundwater research it has proven useful to divide the rocks into two main groups according to the different kinds of flow paths:

porous rocks (media) - fissured (fractured) rocks (media)

The large number of fluids hazardous to groundwater known today are divided into two main groups based on fluid dynamics:

fluids miscible with water - fluids immiscible with water

Of course there are transitional forms between the groups, which shall not, however, be treated here. This report is concerned solely with porous media and fluids which are immiscible with water and mainly with the fluid dynamic principles of their migration.

The migration process of fluids miscible with water has been very well researched in recent years. It is determined mainly by the process of advection and hydrodynamic dispersion. The migration of fluids immiscible with water, with which originally the petroleum people were occupied, is considerably more complicated. The flow in the aquifer occurs at first under the influence of gravity as a cohesive 2-phase-flow, until the immiscible fluid in the pore space is no longer present as a cohesive phase, but disperses into a large number of isolated droplets and attains residual saturation. In this way these fluids become practically immobile under normal conditions and can henceforth only be further transported

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depending on their solubility in groundwater, which is generally weak. For this transport in soluble form the procedures of advection and hydrodynamic dispersion are applied.

The flow processes in the aquifer can be additionally determined in many different ways, according to the type of fluid in question. The following parameters are required for a further evaluation of the flow processes: density, (kinematic) viscosity, vapour pressure (volatility), surface or interfacial tension, physical-chemical characteristics.

The fluids immiscible with water are - as far as the practice of groundwater protection is concerned - chiefly organic substances and for the most part mineral oil products and products of the chemical industry. We will limit ourselves here to a few typical representatives from both groups, of which one possesses a considerably lower density relative to groundwater and the other a considerably higher one.

The schematic presentations in this report were designed on the basis of results of our own model studies and field investigations. During the lecture held at the symposium the migration of both fluids in model troughs were demonstrated by time-lapse photographs of the original laboratory tests. The knowledge obtained can, with certain reservations, be applied to all other fluids immiscible with water.

As a quantitatively very important product group of the chemical industry, whose application outside of chemical plants is broad, the aliphatic chlorohydrocarbons (CHCs) were chosen. Indeed this is a highly topical material group, since it is frequently included with organochlorine-insecticides and polychlorobiphenyls (PCBs) which belong to the halogenated hydrocarbons.

DESCRIPTION OF THE FLUIDS (see Table 1)

To characterize the fluid dynamic properties, the density is chosen as one of the most important parameters. The difference in density compared with that of groundwater determines the level in which the migration in the aquifer takes place. The mineral oil products (for short: oil) are generally considerably lighter than water. Some crude oils very nearly approach the value 1,0 g/ml, however, and certain distillation products of coal (tar oils) reach values of nearly 1,1. The density of the chlorohydrocarbons considered in our investigations lies between 1,3 and 1,6.

Table 1: Density, Viscosity and Solubility of some Chlorohydrocarbons and Mineral Oils

Name, Formula	Density at 20° or 15°C (*) ρ (g/ml)	Kinematic Viscosity at 20°C ν cSt (mm^2/s)	Solubility in Water or Saturation Concentration at 10°C or 20°C(*)(mg/kg)
Aliphatic Chlorohydrocarbons:			
Trichloroethylene C_2HCl_3	1,46	0,40	1.070
Tetrachloroethylene C_2Cl_4	1,62	0,54	160
1,1,1-Trichloroethane $C_2H_3Cl_3$	1,32	0,65	1.700
Methylenechloride CH_2Cl_2	1,33	0,32	13.200 *
Chloroform $CHCl_3$	1,49	0,38	8.200 *
Carbontetrachloride CCl_4	1,59	0,61	785 *
Water	1,00	1,01	
Mineral oil products:			
Medium distillates (light heating oil, diesel fuel)	0,82 to 0,86 *	2 to 8	3 to 8
Petroleum, jet fuel	0,77 to 0,83 *	2 to 4	
Gasoline (Carburettor fuels)	0,72 to 0,78 *	0,5 to 0,7	150 to 300
Crude oils (Africa, Near East, North Sea)	0,80 to 0,88 *	3 to 35	to 25

The viscosity - here the kinematic viscosity ν is appropriately applied as the quotient of the dynamic viscosity and the density - determines the velocity of the flow process, that is, the conductivity K_{fluid} of the porous medium for the fluid in question ($K_{fluid} = k/\nu$). The values imply that in a dry, porous medium CHCs and benzine would flow approximately 3,0 to 1,5 times as fast and light heating oil or diesel fuel approximately 2 to 10 times slower than water. Of course, in water-saturated media the degree of saturation of the immiscible fluids determines their relative flow velocities.

When one speaks of fluids which are immiscible with water, this does not mean that they are absolutely insoluble in water. They usually exhibit a more or less weak solubility, which can be practically meaningless, but only under certain conditions. The solubility (or for fluids which consist of several components, the saturation concentration) of light heating fuel, for example, of about 5 mg/l on the average, is extremely low compared with that of other fluids; in spite of this even such small concentrations can cause groundwater pollution.

The CHCs are highly volatile. For this reason transitions from the atmosphere to surface water and vice versa occur relatively quickly and similarly play an important roll in the transition from the atmosphere to water in the unsaturated zone and vice versa. This is also true of benzine, but not for the mineral oil medium distillates.

The values of the surface tension, which are especially significant for the spreading of a fluid on pure water, are for both CHCs and oils of the same order of magnitude. The surface tension for water/air amounts to 73 dyn cm^{-1} (mN m^{-1}); the values for oil and the CHCs lie mainly between 25 and 32 dyn cm^{-1}.

Of the physical-chemical properties, only the polarity will be mentioned here. CHCs are in general non-polar or weakly polar; oils also consist for the most part of non-polar components. From this it may be concluded that the sorption of dissolved substances in aquifers, which are mainly mineral in nature, must clearly be small. However, for organic soils a significant sorption may be expected.

MIGRATION OF THE IMMISCIBLE PHASE

Whether infiltrating oil or CHCs reach the groundwater table or not, depends decisively upon the infiltration process (e.g. quasi point-formed or areal source, infiltration rate) and upon the retention capacity of the porous medium. The retention capacity for oil in the unsaturated zone lies in general by 3 - 5 l/m^3 in highly permeable media and at the most by 30 - 50 l/m^3 in media of low permeability; for CHCs similar values were found. The heterogeneity of the unsaturated zone (e.g. alteration of different permeable layers) and the degree of water saturation of the individual layers (e.g. so-called "perched" capillary fringes at the boundary of less permeable to more permeable layers) results in a lateral component of the percolation process and consequently a broadening of the oil/CHC-body with increasing depth (Fig. 1). The heterogeneity of the unsaturated zone thus results in general in a considerable reduction of the penetration depth in comparison with that of a homogeneous medium. The retention capacity of the unsaturated zone can therefore only be estimated satisfactorily with a good knowledge of its structure and moisture content. Consequently oil and CHCs behave similarly as a phase in the unsaturated zone, disregarding different percolation velocities as a result of different viscosities.

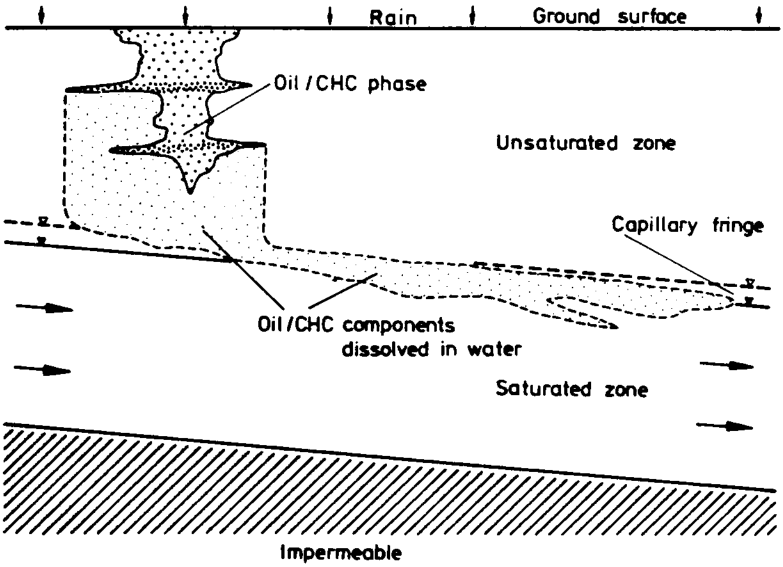

Fig. 1. Oil/Chlorohydrocarbon migration pattern

Oil and CHCs behave fundamentally differently, however, if the infiltrated fluid volume exceeds the retention capacity of the unsaturated zone. Let us first consider the oil (Fig. 2). As soon as the oil reaches the upper boundary of the

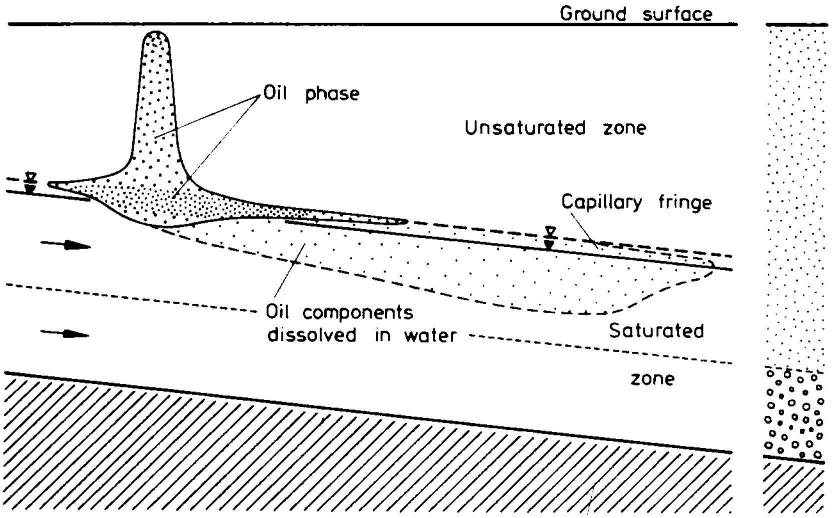

Fig. 2. Oil migration pattern (Schwille 1975)

saturated zone, which lies within the capillary fringe, it spreads out at first downwards as well as laterally, the extent depending on the pressure of the fluid. But the lateral spreading quickly dominates. With decreasing fluid pressure, the oil which was forced beneath the groundwater table tries to reach the surface of the saturation zone again. The tendency of the oil to "swim" up to the surface is so strong that even oil injected beneath the groundwater table does not remain in the saturation zone, except for that part corresponding to the residual saturation (Schwille 1975, Schiegg 1979).

The determining surface for the spreading of the oil is thus within the capillary fringe, where the degree of saturation for water amounts to about 60 - 80 %. The oil clings slavishly to this surface, which in general runs parallel to the groundwater table. The magnitude and form of the area of spreading depends among other things upon the total quantity of oil infiltrated, the infiltration rate, the hydraulic gradient and the hydraulic conductivity of the porous medium in the region of the groundwater table. Fig. 3 provides the general idea.

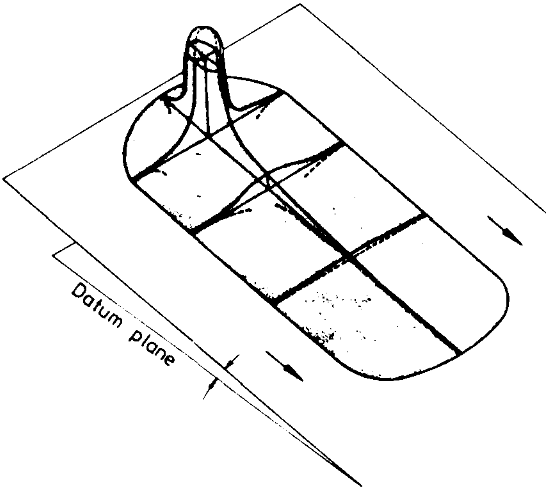

Fig. 3. Surface of the oil body (Schiegg 1977)

In principle the given oil migration patterns (Figs. 1 and 2) are applicable to crude oils too. One should bear in mind, however, that due to the precipitation of compounds from crudes during cooling down under these circumstances, certain crude oils do not behave like Newtonian liquids. Therefore in some cases their migration characteristics in porous media differ considerably from those of petroleum products (Bertsch et al. 1979).

The spreading of CHCs is presented schematically in Fig. 4. When the fluid has reached the surface of the saturated zone the flow is checked as would be expected,

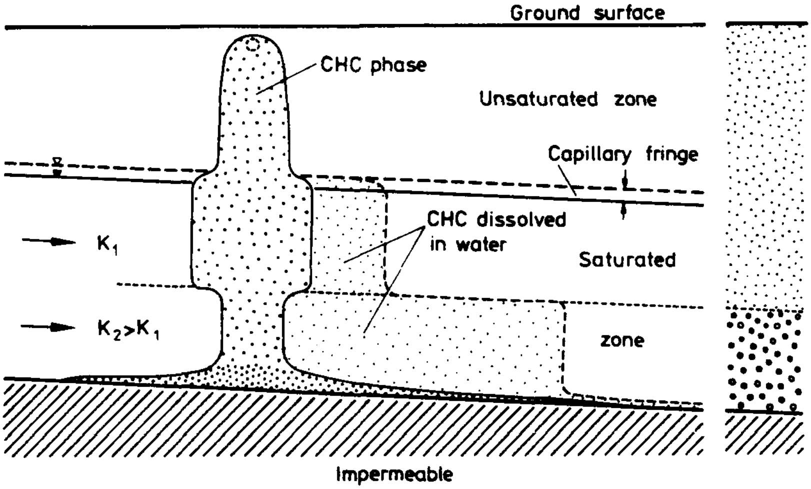

Fig. 4. Chlorohydrocarbon migration pattern

since groundwater must be displaced, but the laterally-effective component is clearly not of such decisive importance. The fluid sinks into the saturated zone. If the retention capacity of this zone is exceeded (this is governed by the residual saturation in the same manner as percolation in the unsaturated zone), then the fluid sinks right to the aquifer bed (the impermeable layer) and spreads out under formation of a more or less flat mound. The spreading out takes place under the pressure head in the mound and follows the aquifer bed as slavishly as the oil over the groundwater table.

On a homogeneous, even aquifer bed the surface of the CHC-mound is similar to that of the oil body on the groundwater table (Fig. 3). In nature, however, the aquifer beds are in no way ideal planes, but have as a rule a more or less undulating relief. The CHCs keep strictly to the deepest parts of the relief, following the local depth contours, whose course in comparison with the groundwater table is usually unknown or not sufficiently known. When the aquifer bed is formed of layers of comparatively low hydraulic conductivity, then an estimate of the form and extent of the CHC "lens" is practically impossible.

The area occupied by the immiscible phase may be calculated for oil for a non-fluctuating groundwater table according to Schiegg (1977). The oil lens would theoretically be fairly thin at its end stage and would have to be correspondingly large. Practice has shown, however, that the areas required by theory are not attained. The reason for this is that because of the seasonally-dependent fluctuations of the groundwater table, the mobile oil still in the spreading stage is distributed in the vertical until eventually, with a certain size of the oil lens a stage of residual saturation and thus immobility of the oil is attained (Fig. 5).

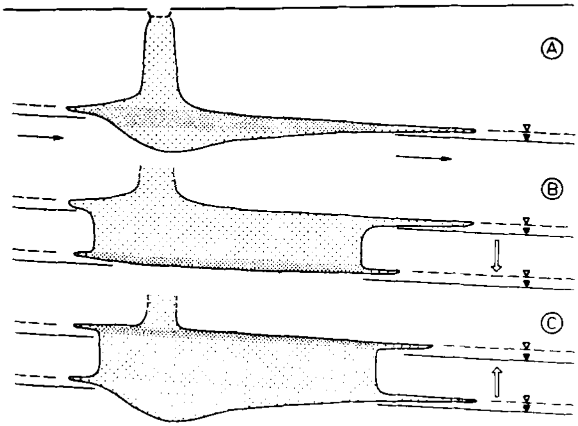

Fig. 5. Oil redistribution in the fluctuation zone of the groundwater table (Schwille 1975)

With the CHCs, which sink to the impervious layer of the aquifer, such a secondary distribution in the vertical is not possible. After the infiltration from above has stopped, the mound so-formed flattens out more and more, until eventually here too residual saturation is reached or until the fluid collects in a depression without an outflow (Fig. 10).

MIGRATION OF DISSOLVED COMPONENTS

The oil/CHC-bodies in which the fluids immiscible with water are found in residual saturation remain penetrable for seepage water as well as for groundwater without serious limitations. The droplets dispersed in the pores result in a good contact with the water into which soluble components diffuse. With the very slow flow-velocities which usually occur, saturation concentration is reached after only a short flow-path. It may thus be derived, that in the lee of a phase body a plume with dissolved components forms (Fig. 6), whose initial concentration corresponds to the solubility or saturation concentration of the fluid in question. The density of these aqueous solutions is usually only slightly raised, so that there is no significant tendency for sinking within the aquifer. Thus the migration of the dissolved substances follows the laws of hydrodynamic dispersion. The distribution of concentration in the plume can be calculated with sufficient exactness with an appropriate estimate of the maximum cross-section of the oil/CHC-body, the hydraulic conductivity and the hydraulic gradient, the coefficients for longitudinal and transverse dispersion and the flow velocity of the groundwater. As an

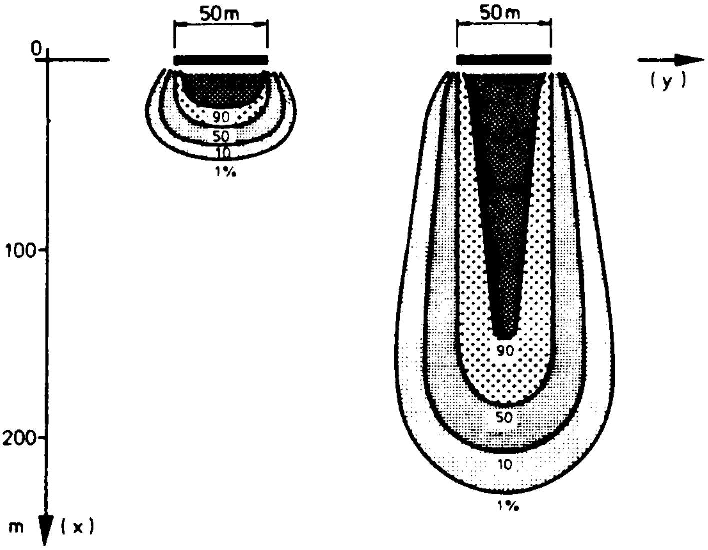

Fig. 6. Concentration distribution of dissolved components as a result of hydrodynamic dispersion. (Left: after 2 months, right: after 12 months; flow velocity: 0,5 m/day)

example for ascertaining the maximum cross-sectional area of an oil body (saturated zone) after practically complete immobility has been reached, Figs. 3, 5 and 7 will serve. Important in this connection is the suggestion that the heterogeneity

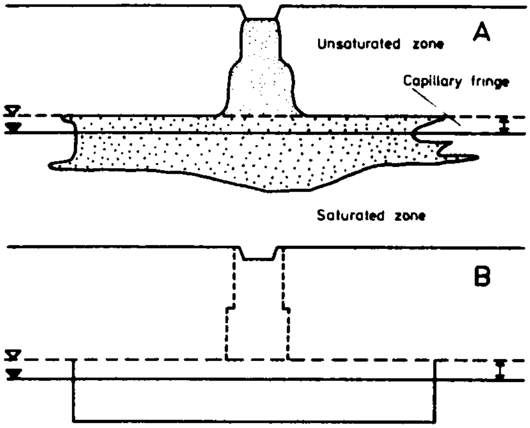

Fig. 7. Cross-section through the oil body perpendicular to groundwater flow direction

of the aquifers, especially multilayered aquifers, shapes the plumes to a much greater extent than would hydrodynamic dispersion alone.

MIGRATION OF GAS COMPONENTS

The high volatility of benzine and CHCs favours a transition of these substances in the pores of the surrounding unsaturated zone. Around the benzine/CHC-bodies an envelope of gas forms with decreasing concentration outwards. In a porous medium with good conductivity this envelope reaches out farthest immediately above the capillary fringe. The evaporation underground is advantageous on the one hand since it provides a considerable contribution to the reduction of the phase in the unsaturated zone, in that the gas is partly released to the open air. On the other hand the gas zone in the pore space results in an additional contact with the percolation water, by means of which again a correspondingly large area of the groundwater can be contaminated.

Gas can even diffuse out of the solution plume in the aquifer into the unsaturated zone, although rather slowly. Even so, by taking advantage of this effect the solution plume may be traced sometimes by measuring the gas concentration with suitable gas-tracing instruments in small bore holes. For mineral oil products with higher boiling points, e.g. light heating oil, the evaporation losses are quantitatively unimportant.

MICROBIAL DEGRADATION

The dissolved oil constituents underground are degraded relatively quickly as long as enough dissolved molecular oxygen is available. Where this is not the case, the degradation takes place anaerobically with recourse to the oxygen of the nitrates and sulphates. The well-known, so-called reduced groundwater type is formed, which converts again to the oxidized type to that extent which the contaminated water mixes with oxygen-bearing groundwater (Schwille 1976). Fig. 8 shows schematically the area of influence of groundwater contamination by degradable materials, as can be deduced from field observations. The form and area of the reduction and oxydation zone can only be properly understood, of course, when the time-

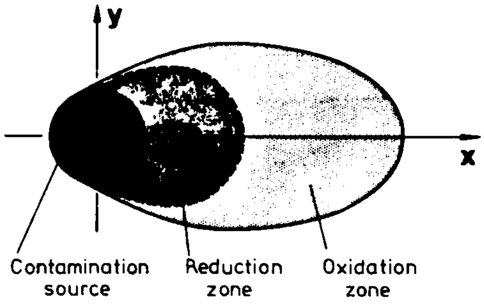

Fig. 8. Schematic presentation of the reduction - oxydation zone (Schwille 1976)

dependent concentration distribution is known as a result of the hydrodynamic dispersion (Fig. 6) and the oxygen content of the uninfluenced groundwater. There is then a critical concentration curve of the soluble substances, within which the admixed oxygen is just no longer sufficient to completely degrade the available organic material aerobically.

In the case of medium distillates, e.g. light heating oil, relatively small concentrations would result in Fig. 6 if the saturation concentration from Table 1 were used to calculate the dispersion plume. In reality, however, through the microbial attack of the oil droplets in the oil body, oil constituents are converted to a large extent into the dissolved form, whereby the source strength is raised. (These intermediate products of degradation are particularly unpleasant with regard to their taste; they involve a higher threshold). Based on the Dutch lysimeter tests (Dietz 1980), we estimate that the microbial degradation of the oil body raises the rate of substances going into solution by at least 10 times the value of the saturation concentration. Instead of 5 mg/l dissolved constituents, for example, about 50 mg/l must be used in the calculation; they degrade, however, at differing speeds. The limiting factor for migration of dissolved oil constituents is the admixing molecular oxygen.

Nothing is yet known about possible microbial degradation of CHCs underground. Such a degradation is not to be expected, however, since CHCs would on the contrary restrict microbial activity. The formation of pronounced reduction and subsequent oxydation zones according to Fig. 8 is therefore not to be expected.

RECOVERY PROCEDURES AFTER POLLUTION

When the groundwater table lies at a shallow depth and the local conditions allow, quick excavation of the oil-polluted ground and pumping out of the oil collecting on the water table may be the most economical solution. For incidents with CHCs on the other hand, it must be carefully examined whether such a measure is justifiable. If the water table lies deeper, then oil or CHCs must be recovered by means of wells. In each case comprehensive investigations are necessary beforehand, which must be strictly adapted to the fluid in question. Figs. 9 and 10 show the basic differences in the type of recovery wells.

With oil, a partially penetrating well suffices; it must be screened in the fluctuation zone of the water table in order to allow the oil entry into the well at any water level. While a stronger pump produces the necessary drawdown of the groundwater table, a weak oil-proof pump can retrieve oil collecting on the water table. This operation with two pumps is continued until the mobile oil is removed; the residual oil cannot be recovered in this manner. If necessary, dissolved constituents can be removed by further operation of the stronger pump.

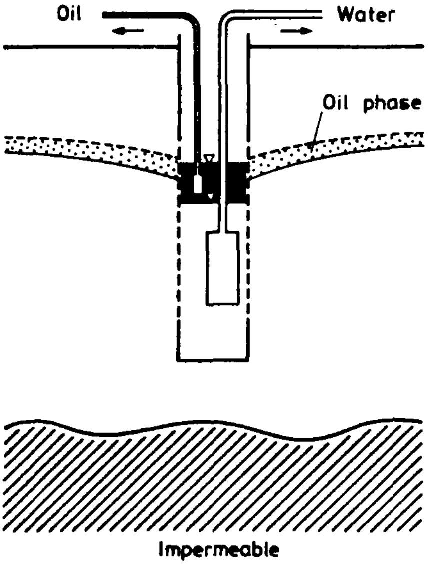

Fig. 9. Oil recovery system, using two pumps

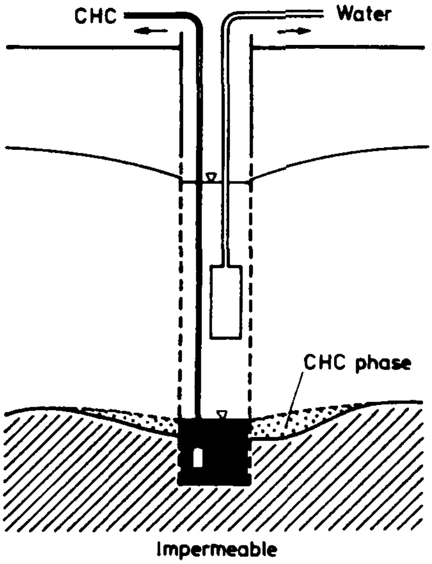

Fig. 10. Chlorohydrocarbon recovery system, using two pumps

With CHC incidents, one must always take into account that a part of the fluid may have reached the bed of the aquifer, as long as larger volumes of fluids are involved. It is important then that the wells fully penetrate into the impermeable layer and are screened to the bottom in order to allow a free passage of the fluid into the sumps of the wells. The fluid which collects there should be recovered with a special CHC-proof pump of low performance or with suitable collecting devices. The stronger pump brings about the drawdown of the groundwater table, not, however, to draw the CHC-phase to the well sump, but in order to remove CHC dissolved in water. The flushing effect is the more effective, the more soluble the fluid. To flush out tetrachloroethylene, for example, one needs, under otherwise the same conditions, about ten times as much water as is required to flush out 1,1,1-trichloroethane (see Tab. 1).

Because of the relatively good solubility of the CHCs as one-component fluids, one has a much better chance of recovering these fluids in the residual stage in a reasonable time than the mineral oil products, which consist of different components of differing and extremely poor solubility except for benzine. Of course, the assumption is that the CHCs have not reached the aquifer-bed or at least not in large quantities. In extreme cases the quantity of CHCs that are retained in the pore space can be very small in comparison with that lying on the aquifer-bed. If this has collected in a despression without an outflow, it can be removed in dissolved form only over an extremely long period. It is clear that in such a case the groundwater contamination may also be correspondingly small.

The discharged water contaminated by CHCs cannot in most cases be fed into surface waters or sewers without further treatment. Filtration over activated charcoal, possibly after preceding aeration, could be a practicable but rather expensive method of decontaminating the water, and could be used to recharge the groundwater. The necessary hydraulic methods for optimizing the discharge/recharge process are well known.

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