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Descripton Notes

2. ON-SITE TREATMENT METHODS BASICALLY AVAILABLE

2.1 General

Basically, the following on site treatment methods are available:

- Extraction (leaching)
- Thermal treatment
- Chemical treatment
- Phase separation
- Steam-stripping
- Micro-biological treatment
- Flotation

2.2 Extraction (leaching)

2.2.1 Introduction

The extraction process of contaminated soil basically consists in mixing the contaminated soil with an extracting agent to transfer the contaminants from the soil particles to the extracting agent. With this mixing step it is possible to remove not only contaminants that are soluble in the extracting agent (in general an aqueous solution, sometimes an organic solvent), but also contaminants which are in fact insoluble in the extracting agent.

In the latter case it is a requisite that the extracting agent has properties that are favourable to form stable colloidal suspensions of the contaminants. After extraction the purified soil particles are separated from the extracting agent containing the contaminations. These are subsequently removed from the extracting agent.

2.2.2 Processscheme and description

A complete scheme of the extraction process for the treatment of contaminated soil is given in figure 1. After excavation the soil is passed over a wide-mesh screen to separate large objects therefrom. Large clods of soil are reduced in size. The soil is then transported to the extractor where soil and extracting agent are mixed intensively. After extraction, soil and extracting agent are separated. The soil is subjected to a post-treatment to remove remaining extracting agent and/or contaminants. This can be done by washing, neutralisation, evaporation and so on, dependent on type of contaminations, type of extracting agent and type of soil. The extracting agent leaving the extraction apparatus generally contains the finest soil particles. To remove these particles a second separation step can be necessary. The fine particle fraction thus obtained is also subjected to a post-treatment. The extracting agent leaving the second separation step is treated to remove the contaminations. These contaminations are usually separated as a concentrated sludge which has to be incinerated or disposed of elsewhere.

There are several modifications of the extraction process, dependent on the type of soil to be treated and the type of contaminations to be removed. The following types of equipment can be considered:

Pre-treatment:

- Crusher
- Sieve

Extraction:

- Mixer/settlers in line
- Screw extractor
- Fluidised bed
- Hydrocyclones and settlers in line
- Sieve belt

Separation of soil and extracting agent:

- Settlers
- Tiltable plate separators
- Vacuum belt filter
- ~ Hydrocyclones
- Centrifuges
- Rotating sieves

Post-treatment of soil:

- Vacuum belt filter with a washing installation

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- Screen with a washing installation

Separation of fine particles:

- Centrifuges
- Hydrocyclones
- Sedimentators

Treatment of extracting agent:

(in case of water as extracting agent)

- Coagulation/flocculation/settling/dewatering of the sludge
- Ion exchange
- Activated carbon adsorption
- Reverse osmosis
- Ultrafiltration
- Chemical conversion (ozon, hydrogen peroxide)
- Electrochemical conversion .
- Stripping
- Precipitation
- Flotation

(in case of an organic solvent as extracting agent)

- Evaporation
- Distillation

2.2.3 Potential applications

Heavy metals

For the removal of (heavy) metals from contaminated soil the following extracting agents can be considered:

-	HC1	(Cd,	Cu,	Zn,	Ni,	Cr,	As,	SЪ,	Pb)
-	H ₂ SO ₄	(Ca,	Cu,	Zn,	Ní,	Cr,	As,	Sb)	
-	HNO3	(Cd,	Cu,	Zn,	Ni,	Cr,	As,	SЪ,	Pb)
-	NaOH	(Pb,	Zn)						

It is also possible to make use of complex-forming agents, pure or in combination with acid or lye. Also combinations of lyeextraction and acid extraction can be necessary.

Cyanides

For the removal of cyanides or cyanide complexes aqueous NaOH can be used.

Hydrocarbons

Extraction of hydrocarbons can be achieved either by using an aqueous solution of HCl, NaOH or Na_2CO_3 or an organic solvent. The application of aqueous NaOH- or Na_2CO_3 -solution is based on the fact that these types of solutions have disperging properties and are able to solve humic-acid like substances present in the soil. This makes it possible to remove contaminations from the soil that are insoluble in water. As regards the use of organic solvents it should be noted that the soil to be treated generally contains a small amount of water. This means that extracting agents are preferred which can dissolve the water present in the soil. In this context methanol, ethanol, isopropanol and acetone can be mentioned as suitable extracting agents.

Halogenated hydrocarbons

In general the same extracting agents can be used as mentioned for hydrocarbons.

2.2.4 Bottlenecks

The extraction process has favourable possibilities of application if the soil to be treated only consists of sand particles, but unfortunately this is seldom the case. Mostly also organic, humicacid like substances and also clay particles are present.

The presence of organic humic-acid like substances can result in the following bottlenecks:

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- Heavy metals (but also organic contaminations) are preferably adsorbed or absorbed by humic-acid like substances. Extraction with acids can be difficult in that case. For the removal of organics lye extraction is often more effective than acid extraction. However, in general a large part of the humic-acid substances dissolves in lye resulting in large amounts of sludge being formed when the extracting agent is purified. It is extremely difficult to separate the contaminated compounds from the humicacid like substances.
- The amount of extracting agent to be used for extraction of the contaminants can increase strongly if large amounts of humic-acid like substances are present.

The presence of clay particles gives the following problems:

- Clay particles cannot be separated effectively from aqueous extracting agents by means of simple separation techniques such as settling.
- Clay particles have strong adsorption properties with respect to heavy metals.
- If clay particles are not removed and purified in a post-treatment process, they concentrate in the sludge resulting from treatment of the extracting agent. The result can be a substantial amount of contaminated sludge which cannot easily be disposed of.

Organic extracting agents have to be removed completely from the treated soil.

2.2.5 General remarks

To obtain an efficiently operating extraction process, counter current flow of extracting agent and contaminated soil is a prerequisite.

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2.3 Thermal treatment

2.3.1 Introduction

Thermal treatment of soil essentially comprises three different modes of operation, i.e.: -

- Thermal treatment of soil by direct heat transfer from heated air, (or an other gas) with the aim to evaporate the contaminants and carry them off with the gasphase.
- Thermal treatment of soil by indirect heat transfer, with the aim to evaporize the contaminants and to carry them off with the gas phase.
- Thermal treatment of soil by a direct heat transfer from a heated gas or by direct incineration with the aim to destruct the contaminants to harmless products.

Post-treatment of the gas leaving the heat treatment appliance can be achieved in three different manners, i.e.:

- Incineration at high temperatures in an after-burner.
- Thermal treatment at moderate temperatures using appropriate catalysts.
- Treatment at low temperatures by wet scrubbing of the gas and purification of the washing liquid.

In the following the different principles of operation will be discussed in more detail.

2.3.2 <u>Thermal treatment by direct contact with heated air with the aim</u> to evaporate the contaminants

2.3.2.1 Processscheme and description

In figure 2 a scheme is shown of this mode of soil treatment. The three alternatives of post-treatment of exhaust gases are included.

Treatment of soil at high temperatures in order to evaporate the contaminants by direct contact with heated air can be effected in a kiln, mostly a rolary kiln. In the rotary kiln temperatures of up to 600°C and higher are possible. Volatile contaminants and water originally present in the soil will be evaporated. The air supplied to the rotary kiln is raised to a high temperature in a heater. Because of its relatively low heat content, a large amount is necessary to provide the energy for elevating the temperature of the soil to about 600°C or higher.

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The gas leaving the rotary kiln will pass a cyclone for separation of the fine mineral particals transferred by the exhaust gas flow. During passage of the cyclone the gas should have a sufficiently high temperature to avoid condensation of contaminants on the fine mineral particles to be separated.

For further treatment of the gas three possibilities exist:

Incineration at high temperatures (I)

The temperature of the gas leaving the cyclone is elevated to a value high enough to destruct the contaminants to harmless products. In some cases temperatures up to 1400°C are necessary. The incineration can be effected in an after-burner where a residence time of several seconds is possible and where excess oxygen is present.

- Thermal treatment at moderate temperatures, using proper catalysts (heterogeneous catalysis) (II)

Destruction of the contaminants can basically be realized by using the proper catalysts. Catalytic oxidation is an alternative to incineration in an after burner. In principle it is possible to oxidize catalytically several organic substances at temperatures between 200 and 400°C, which substances would otherwise only be destructed at temperatures of 800°C and higher. In general, for heterogeneous catalysis metals like Ni, Zn/Cu, Fe/Cu, Al/Cu, Pd/C are applicable.

Treatment at low temperatures (III)

By this method the gas from the cyclone is cooled in an air condenser and then scrubbed with a suitable liquid. It may be possible that very fine particles which have even passed the cyclone will be retained in the liquid phase. The liquid used must be such that the condensed contaminants tend to solve in it, or to be retained as a colloidal suspension. The spent liquid may be partly recycled and partly used for further treatment. In case the liquid is an organic solvent this treatment step may consist of a distillation step. The scrubbed air can be polished, e.g. by activated carbon adsorption, and then be discharged.

2.3.2.2 Potential applications

Evaporation of contaminants

Evaporation of contaminations by thermal treatment of the soil is restricted to those cases where the contaminants have relatively high volatilities at the applied temperature. So, the mode of operation is applicable for removing hydrocarbons and halogenated hydrocarbons which have high volatilities. Moreover, the method can be applied for the sublimation of certain metals or metalcompounds.

Post-treatment of gas

Incineration of the spent gas leaving the cyclone is particularly favourable when hydrocarbons are involved which completely decompose at the applied temperatures. Incineration of halogenated hydrocarbons is a possibility only when emission of the evolved halogenides to the environment is admitted. If not, the halogenides have to be absorbed by a washing liquid (water) before emission of the spent air is permitted. In the case of heavy metals, post-treatment of the gas by means of an after-burner has always to be followed by a.process that removes the heavy metals from the gas phase.

It is evident that catalytic oxidation of the contaminants present in the spent air is applicable to those cases where the contaminants are oxidizable to harmless oxidation products at the applied conditions. In the case of halogenated hydrocarbons catalytic oxidation has to be combined with gas-washing.

Treatment of the spent gases at low temperatures in a scrubber may be the most generally applicable mode of post treatment. With this method all remaining contaminants, such as heavy metals, As, Sb and halogens can be removed from the gas phase, if the proper equipment

2.3.2.3 Bottlenecks

The most important bottlenecks which can be encountered in the thermal treatment of soil by means of the above mentioned process - evaporation of the contaminants by contacting the soil with a hot gas stream followed by treatment of this gas stream - are:

- A relatively large amount of air is necessary for transferring the heat required for evaporation in the rotary kiln. Consequently, the installation for treatment of the spent gases has large dimensions (heat exchanger, after-incineratory scrubber, catalytic oxidation equipment). This means high 'investment costs.
- The process requires a large amount of energy due to the fact that mostly a lot of water has to be evaporated and that the soil itself has a large heat content at elevated temperatures.
- The practical use of the principle of catalytic oxidation is still in its preliminary stage.
- Incineration should occur at such process conditions (temperature, residence time) that formation of toxic components (e.g. dioxines) is avoided.

2.3.3 <u>Thermal treatment by indirect heat transfer, with the aim to eva-</u> porate the contaminants

In figure 3 a scheme is shown of this mode of evaporation of the contaminants. The essential difference, as compared with the process mentioned in 2.3.2, is that heat transfer is realised indirectly, e.g. by the use of heat transfer pipes in a rotary kiln. Only a small gas stream is necessary for the transport of the evaporated contaminants out of the kiln. The post-treatment of the relatively small gas stream leaving the kiln occurs in a same manner as discussed in 2.3.2. However, due to the smaller gas stream the dimensions of the post-treatment installation are markedly smaller, resulting in lower investment and process costs.

The applicability and restrictions are the same as mentioned before in 2.3.2.

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Concerning the typical bottleneck of this treatment process, it has to be noted that heat transfer from a hot gas by an indirect method, requires very large dimensions of the heat exchanger. This is mainly due to the low heat transfer coefficients that can be obtained. Consequently the investment costs of the heat exchanger/kiln are relatively high.

For other bottlenecks that can be encountered, reference is made to 2.3.2.

2.3.4 <u>Thermal treatment by direct heating or incineration, with the aim</u> to destruct the contaminants.

The thermal treatment methods, mentioned in 2.3.2 and 2.3.3 are particularly applicable if the contaminants to be removed from the soil have a relatively high volatility at the applied temperatures. In both processes the volatile contaminants are evaporated and then destructed or otherwise separated from the gas phase. An other possibility of thermal treatment of contaminated soil is direct incineration at a temperature necessary for destruction of the contaminants. This can be achieved in a rotary kiln, too. Figure 4 gives a scheme of this process. It has to be noted that post-treatment of the spent gases can occur in a manner already discussed in 2.3.2 and 2.3.3.

Destruction of contaminants present in the soil by incineration or direct heating can be applied if the contaminants are of an organic nature and have a low thermal stability. It can be used both for high volatile organic components and for organic components with low volatility, even at bigher temperatures.

In general incineration processes are carried out at temperatures between 700 and 1200°C. A special problem in treating contaminated soil in an incinerator is that vitrification or sintering of the mineral part of the soil can occur at high temperatures. To prevent vitrification and sintering of soil particles it is essential that the incineration temperature is as low as possible and the soil particles are in continuous motion with respect to each other.

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This can be achieved in a rotary kiln or in a fluidized bed. In the latter case however, it is a pre-requisite that the soil to be treated should have fluidizing properties when it is in a dry state.

For a brief discussion of the various process steps which can be distinguished with this type of treatment process and the typical bottlenecks of thermal treatment, reference is made to 2.3.2 and 2.3.3.

2.4 <u>Chemical treatment</u>

2.4.1 Introduction

Chemical treatment methods comprise a large number of techniques with the common feature of a chemical reaction (directly or indirectly) taking place between the contaminants and a chemical agent and resulting in harmless products. The methods discussed here do not include immobilisation techniques (e.g. calcination), for these are not considered as actual cleaning-up methods.

Two major fields of chemical treatment methods are to be distinguished. First, the treatment of the soil in a dry form and secondly the treatment of soil in suspension (in a suitable liquid) with a suitable chemical. Besides for a direct treatment of contaminated soil chemical treatment methods can also be applied in combination with other, e.g. thermal treatment and extraction. For instance in the case of extraction, chemical treatment can be of importance for the detoxification of the used and polluted extracting agent.

Basically a large number of chemical treatment methods for contaminated soil are available. The following table gives an impression of the most important chemical treatment methods for hazardous industrial wastes and the presumed applicability to contaminated soils.

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Treatment method	Applicability to_contaminated_soil
electrolysis 1) chlorinolysis 2)	low low
neutralisation hydrolysis 3)	high moderate
chemical oxidation	moderate
chemical reduction	moderate
ozonation 4)	low
photolysis ⁵⁾	low

Notes:

- Electrolysis refers to the reactions of oxidation or reduction taking place at the surface of conductive electrodes immersed (in a suspension of soil) in an electrolyte, under the influence of an applied EMF.
- 2) Chlorinolysis refers to the reactions between hydrocarbons and chlorine at temperatures around 500°C and pressures of about 200 atm. forming carbontetrachloride.
- ³⁾ Hydrolysis generally refers to double decomposition reactions with water of the type: XY + $H_2^0 \rightarrow HY$ + XOH. The reactions are usually carried out at elevated temperatures and pressures, often with acid, alkali or enzyme catalysts.
- ⁴⁾ Ozone gas is a powerful oxidizing agent that cannot be shipped or stored, so it must be generated on site prior to use. The ozone produced is led through a suspension of soil in water or a packed soil bed.
- 5) In photolysis, chemical bonds are broken under the influence of UV or visible light. Reactor geometry must be such that adequate penetration of the light into the contaminated soil is allowed.

Not all techniques will be considered in the following paragraphs. Based on the limited applicability of chlorinolysis and photolysis, these will not be discussed any further.

Some general characteristics of the chemical treatment methods of soil are:

- An intensive contact between soil and chemicals is needed;
- Contact times are frequently long;
- Chemicals are dosed in excess of the contaminants to ensure complete detoxification.

2.4.2 Processschemes and description

Only some general processschemes will be given, because of the large number of alternative methods and the lack of experience in applying these techniques to soil. Nor will attention be given to chemical methods in post-treatments.

The first group of processes are those which simply consist in a mixing step of contaminated, relatively dry soil with a chemical (figure 5). As noted before, the chemicals will be added in excess, and therefore this method can be used only when the chemical itself is harmless to the environment or quickly looses its chemical stability. It is desirable that the soil be rather dry after the treatment before it is re-deposited, and so the chemicals should be added in a solid form or as liquid in a minor volume ratio to the soil. An important example of this kind of treatment methods is pH-adjustment of soil. For the mixing step several kinds of apparatus can be used, for instance rotating mixers and screw conveyers.

A second group of processes comprises techniques in which a separation step between soil and chemicals is needed (figure 6). This can be the case with chemicals in solution (e.g. diluted sodium hypochlorite) or gases (e.g. ionised air, ozone). In these processes soil is brought into contact with a suitable chemical reagent. After a certain reaction time in the mixer/reactor the mixture is fed to a separator, where the soil is separated from the reactive phase as completely as possible.

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In some cases, upgrading of the reactive phase may be possible, otherwise the used chemicals should be detoxified and discharged. Upgrading of the reactive phase generally results in a waste stream of reacted matter and sometimes some soil particles.

The treated soil generally needs a post-treatment to remove or detoxify any hazardous material present (either the contaminants or the used chemicals). This will also result in a waste stream in most cases.

The following type of equipment can be considered:

Mixer/reactor:

- Rotating mixer
- Screw conveyer
- Scrubber

- Rotating mixer

gas-phase chemicals

liquid-phase chemicals

- Bubble column

Separators:

- Settler
- Tiltable plate separator
- Centrifuge
- Sieve

Apparatus for upgrading used chemicals:

- Chemical reactor
- Distillation column
- Precipitation tank

Apparatus for post-treatment:

- Washing or rinsing devices
- Stripping devices
- Drying/evaporation devices
- Chemical reactors

The first and the second group of processes (figures 5 and 6) comprise treatment methods such as neutralisation, hydrolysis, che-, mical oxidation and reduction and ozonation, of which especially ozonation, chemical reduction and hydrolysis are deficient in practical knowledge towards soil decontamination.

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A third group somewhat different from the first two is electrolysis. Figure 7 shows the processscheme.

It is not known if this process can be applied directly to a mixture of soil and a suitable liquid phase. In any case one can assume that electrolysis is a suitable technique as a secondary treatment step of, for example, extraction liquids. In the latter case one can think of reclaiming heavy metals and the destruction of (halogenated) organic compounds.

2.4.3 Potential applications

The chemical methods considered are derived from treatment methods for hazardous wastes in general and have not yet been developed and adapted to treating contaminated soils. Therefore the following list of applicational fields of chemical treatment methods is probably not exhaustive and furthermore too optimistic in some cases.

Contaminant	Treatment_method	Chemicals that can be used
Cyanide	. Oxidation to CNO ⁻ and . Hydrolysis to CO ₂ + NH ₃ or N ₂	. NaClO, Ca(ClO) ₂ . Cl ₂ , alkalí
Heavy metals	 Oxidation to change leachability (e.g. Cr³⁺ → Cr⁶⁺) or to enhance precipitation 	. NaClO, KMnO ₄ , O ₃ , H ₂ O ₂
 	. Reduction (e.g. Cr ⁶⁺ → Cr ³⁺ TElectrolysis). SO ₂ , SO ₃ ⁻ , Zn
Halogenated hydrocarbons	. Hydrolysis	. aqueous acids, alkali
	. Oxidation	. с10 ₂ , 0 ₃ , H ₂ 0 ₂ , КМПО ₄

Contaminant	Treatment_method	<u>Chemicals that</u> can be used
Organics, general	. Oxidation (e.g. phenolics, aldehydes)	. H ₂ 0 ₂ , 0 ₃
	. Hydrolysis . Electrolysis	. Acids, alkali

2.4.4 Bottlenecks

As mentioned before, none of the chemical methods that can be considered for application have yet been developed for treating contaminated soils. Therefore much research and development work is needed.

The following bottlenecks are expected:

- Natural soils consist of several compounds among which there are many of an organic nature (humic-acid like substances). Chemicals added to contaminated soil will often also attack these natural compounds. It is possible that the products resulting from these reactions are not acceptable from an environmental point of view.
- A long reaction time will often be needed to ensure that all contaminants are completely converted. Therefore large reactors will be required for on-site treatment.
- Chemical agents are expected to be used in excess, which is due to competitive reactions and to ensuring a terminating reaction.
 Mostly, the used chemicals are not harmless to the environment, so an extra separation and post-cleaning step are needed.

2.5 Phase separation

2.5.1 Introduction

Treatment techniques for contaminated soil that are based on a phase separation between the original soil particles and the phase consisting of solid or liquid contaminants, can be divided into the following groups:

 Separation based on differences in specific gravity. Especially contaminants that have a lower density than water can be separated from soil by adding a sufficient quantity of water.

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- Separation based on differences in particle size. When the contaminants consist of a powder-like material which differs in size from the other soil particles, separation can be carried out by sieving, either wet or dry.
- Separation by making use of differences in settling velocity in a suitable liquid (or sometimes a gas phase).
- Separation on the basis of different magnetic properties. When the contaminants are found in particles with magnetic properties, separation is possible by applying a magnetic field.

2.5.2 Process description and potential applications

2.5.2.1 Separation based on differences in specific gravity

A schematic presentation of this treatment method is given in figure 8. The process comprises a treatment step where contaminated soil and a suitable liquid (in most cases water) are intensively mixed. Mechanical means such as water jet-, water/air jet- and scrubbing devices can be used in this mixing process. After mixing the soil phase is separated from the water phase. The latter contains the contaminants. The contaminants are separated from this water phase as a sludge or liquid. The purified water phase can be re-used. The separator can be designed as a two-stage separator, for example the first stage for separating the cleaned soil from the contaminated water and the second stage for the separation of water and contaminants.

This process is particularly applicable to the treatment of sandy soil contaminated with oil or other substances with lower density than water and not soluble in water.

2.5.2.2 Separation based on differences in particle size

The process scheme given in figure 9, consists of a sieving device for wet (or dry) sieving. In the case of wet sieving post-treatment of the soil is required for dewatering.

Sieving devices are commercially available in a wide variety and do --not need further explanation. The same holds for dewatering screens in the case of wet sieving as a separation technique. As mentioned before it is necessary that the contaminated particles should have a particle-size distribution within a relatively narrow range in order to ensure a sufficiently small waste stream or mass stream for secondary treatment.

Dry sieving can be applied down to about 100 μm when the soil is sufficiently dry, otherwise larger mesh sizes must be used. Wet sieving is possible down to about 30 μm .

Fields of application are for instance soils contaminated with hazardous particles.

2.5.2.3 Separation based on differences in settling velocity

Figure 10 schematically shows a treatment technique that is based on differences in settling velocity. The process consists of a wet or dry classification step where the soil particles and the contaminants are separated. The liquid or gas flow carrying the contaminated particles is treated in a second process step in which the contaminants are removed. In the case of dry classification the soil must first be dried.

The kind of apparatus to be used for the classification process depends on the range of particle sizes to be separated and on the phase (liquid or gas) used for classification.

Types of apparatus for liquid-based classification (water):

- Upflow column or jet sizer (countercurrent flow)
- Screw classifier
- Rake classifier

Types of apparatus for gas-based classification (air):

- Zigzag air classifier (countercurrent flows)
- Cross-flow classifiers.

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The classifying technique is applicable to sandy soil with the contaminants present as particles having settling velocities different from the settling velocity of the soil particles.

2.5.2.4 Separation based on different magnetic properties

The separation technique based on the magnetic properties of the contaminants-containing fraction in soils is basically simple. The contaminated soil is slurried up with water and then passed through a magnetic field (see figure 11). A technique that can be used is High Gradient Magnetic Separation (HGMS).

The applicability of this technique is probably limited. The most important group of contaminated soils to be treated by this technique is soil containing iron or magnetite particles which are doped with hazardous materials (heavy metals).

2.5.3 Bottlenecks

The most important bottlenecks in the above mentioned treatment processes is the presence of clay particles (difficult to separate from the water phase). The presence of humic-acid like substances can hinder the settling of particles and contaminations present in the liquid adhering to the soil particles.

2.6 Steam-stripping

2.6.1 Introduction

Steam-stripping basically consists of a process in which volatile components are removed from a solid or liquid phase by contacting it with steam that carries off the volatiles. The process can be applied for cleaning up contaminated soil if the contaminants to be removed are more or less volatile. These contaminants may be either water soluble or water insoluble. To obtain an efficient treatment process it is important that the volatility of the contaminants is high enough and an intensive contact between gas and solid is guaranteed.

2.6.2 Processscheme and description

The equipment used for steam distillation in waste treatment generally consists of a rotating drum in which soil and steam are in counter-current flow. The soil is heated directly by the superheated steam. The evaporated contaminants are carried off with the steam flow. Steam and contaminants are both condensed in a condenser. The contaminants are then separated from the condensate. Several treatment methods are available, dependent on the type of contaminants. Activated-carbon, adsorption, simple decantation of the contaminants which are water-immiscible and centrifuging can be mentioned in this context. In figure 12 the process is presented schematically.

2.6.3 Potential applications

The types of volatile contaminants that can be removed from contaminated soil include:

- Water immiscible hydrocarbons such as:
 - . petrol
 - . kerosine
 - . terpentine
 - . benzene
 - . toluene
 - . xylene

- Water-immiscible halogenated hydrocarbons such as:

- . perchloro ethylene
- . trichloro ethylene
- . methylene
- . trichloro benzene
- . dichloro benzene.

- Water-soluble hydrocarbons such as:

- . methanol
- . ethanol
- . iso-propanol
- . phenol.

2.6.4 Bottlenecks

None of the above mentioned potential applications have yet been developed for practical purposes of soil cleaning. Much research work has still to be carried out. This work should be focussed on the following bottlenecks:

- Contaminated soil mostly contains some water. It is therefore expected that the soil has poor free-flowing properties. This can be a problem in effecting an intensive contact between soil particles and steam flow.
- When no energy is recovered the total energy need of the process can be high. Recovery of energy is possible if vapour recompression is applied.
- It may be possible that very fine particles will be carried off with the steam and are separated in the condenser. This can cause problems if water and contaminants have to be separated.

2.7 <u>Micro-biological treatment</u>

2.7.1 Introduction

Basically, many hazardous chemicals present in soil can be destructed to harmless components such as H_2O and CO_2 by micro-biological methods. To effect microbiological degradation in a actual situation of soil contamination a number of conditions has to be fulfilled. These are:

- The presence of sufficient oxygen
- The presence of nutrients (P and N)
- The presence of sufficient water
- Concentrations non-toxic to the micro- organisms present in the soil
- The presence of the appropriate micro-organisms.

In general micro-biological degradation processes are very slow. This is especially the case with anaerobic degradation processes. Aerobic micro-biological degradation processes mostly proceed much faster. This means that for on-site treatment of contaminated soil only aerobic micro-biological processes of contaminants that can be easily degradated are applicable.

2.7.2 Process description, applicability and bottlenecks

Several modifications are possible for the microbiological treatment of contaminated soil. A schematic presentation of the basic process scheme is given in figure 13. The soil to be treated is mixed up (for example in a rotating drum) with nutrients suitable micro-organisms and water (if necessary). After mixing the soil is supplied to an aerated reactor. In this reactor, which can be a simple container, microbiological degradation of the contaminants takes place.

The method is generally applicable to all contaminants which, under certain circumstances, are biodegradable. A pre-requisite for onsite application in a mobile installation is that the microbiological conversion rate of the contaminants is fast enough. Otherwise a long residence time and consequently a large reactor volume are necessary. This can make the method impractical for actual clean up operations. The requirement of fast microbiological conversion of the contaminants strongly limits the applicability of on-site biodegradation methods.

It should be remarked that it may be allowed in some cases to redeposit the soil - mixed with micro-organisms, water and nutrients before the microbiological degradation has been concluded. In such cases lower microbiological degradation rates are acceptable. This means that anaerobic micro-biological degradation processes can be applied too.

2.8 Flotation

Flotation is a process for separating certain types of particles from suspensions. Flotation processes are widely used, particularly in ore processing. In the case of soil treatment the process can be applied for the selective removal of contaminants from a suspension of contaminated soil in water. A pre-requisite, however, is that the contaminants are present as distinct liquid or solid particles. The flotation process basically consists of three steps:

- Treatment with a suitable chemical
- Flotation
- Removal of concentrated contaminants and post-treatment.

The first step involves a treatment in which suitable flotation agents are added to a suspension of contaminated soil in water. These agents should adhere selectively to the contaminated particles and their function is to give hydrophobic properties to the surface of the contaminants. This first step mostly requires an intensive mixing of contaminated soil, water and flotation agents.

The second process step consists in the formation of small air bubbles in the soil suspension. These air bubbles adhere to the hydrophobic particles of contaminants and transport them to the surface of the suspension. The concentrated contaminants in the surface layer are removed after which the layer is dewatered. In general this results in a concentrated sludge of the contaminants.

In figure 14 the process scheme of the complete flotation process is shown.

As already mentioned, the common mode of selective flotation is basically applicable where the contaminants are present in the soil as distinct particles. If this condition is satisfied all kinds of contaminants like halogenated organics and metal compounds are treatable in this way. However, there is also an other mode of flotation - so called ion-flotation - that can be applied to remove inorganic ions from a soil-water suspension. The flotation reagents used for ion-flotation exist as ions in an aqueous solution. In a suspension of contaminated soil they react with the contaminating ions to form components with hydrophobic properties. These components can easily be lifted out from the suspension by means of air bubbles. Ion-flotation is applicable where dissolved metals like Cu, Co, Cd, Ni, etc. are present in the soil suspension. Although for example separation of dissolved copper from ore by ion flotation has been investigated, the principle has not yet reached the stage where it can be applied in actual practice, not even in ore mining.

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3. PRACTICAL EXPERIENCE

3.1 General

The most characteristic aspects of the on-site treatment processes potentially available for the treatment of contaminated soil are discussed in chapter 2 and are summarised in the table. In this table an attempt has also been made to estimate the possibilities of developing the mentioned processes to the stage of practical application. It should be noted that the table only gives a first rough qualification. Further experimental investigations and studies are necessary to evaluate the several treatment processes in more detail.

The table clearly shows that at this moment only a minority of the mentioned processes has already been developed, tested or applied for the on-site treatment of contaminated soil. In fact only one process - evaporation of the contaminants from the soil and treatment of the gases in an after-burner - has been applied in an actual clean up operation of a former gas work site in the Netherland (at Den Helder). Investigations have also been carried out on the extraction of contaminated soil. In the Netherlands both the extraction of organic bromine compounds (at Wierden) and the extraction of cyanides (at Den Haag) from contaminated soil have been investigated successfully on a pilot plant scale. In paragraphs 3.2, 3.3 and 3.4 the experiences with these processes are discussed more in detail.

As regards most of the other potential processes for cleaning up contaminated soil, the following remarks have to be made:

- Some of the mentioned processes have already been applied for treating hazardous waste materials. This is especially the case with thermal treatment processes. The experiences with these processes can be extremely valuable in developing processes for the treatment of soil contaminated with hazardous wastes.
- In most cases of soil contamination very large amounts of soil have to be treated. This means that only short residence times of the soil in the on-site treatment installation are allowable.

- The specific properties of soil such as particle-size distribution, percentage of clay particles and humus-like substances, and the total percentage of organics have a very strong influence on the type of treatment process that can be applied.
- Except for a few, most of the treatment processes mentioned in the table result in a residual hazardous waste. In most cases the amount of this waste fraction is only a few percent or less of the total amount of treated soil. If a treatment process produces a larger amount of waste the process becomes proportionally less attractive.
- In developing on-site treatment processes for actual application the technological know-how already mentioned in the introduction can be relevant (know-how concerning unit operations, hazardous waste treatment, treatment of waste water, transport and handling of soil).
 Also the typical proporties of soil and the contaminants are important factors in developing on-site treatment processes.
- From an economic point of view each type of soil contamination will require its own specific treatment process, adapted to the specific properties of soil and contaminants. This means that for a particular clean-up situation an investigation into optimum process and process condition has to be carried out.

3.2 <u>Removal of organic bromine compounds (laboratory and pilot plant scale</u> investigations) .

A site in the municipality of Wierden (the Netherlands) is contaminated with several aliphatic bromine compounds, such as tetrabromo ethanes, dibromo butanes and dibromo decane. This site, containing about 30.000 tons of soil and with a concentration of contaminants varying between ten and several thousands of mg bromine per kg of soil, is a threat to the ground water used for the production of drinking water. By order of the Ministery of Public Health and Environmental Protection TNO and HBG* investigated a number of cleaning-up techniques.

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HBG: Hollandsche Beton Groep N.V., P.O. Box 81, 2280 AB Rijswijk, The Netherlands.

Experiments on a laboratory scale were carried out to assess the possibilities of cleaning-up techniques such as:

- a) Extraction with 1,1,1 trichloro ethane and aqueous solutions of:
 - Soft soap
 - Na_2CO_3
 - NaOH
 - NaClO
- b) Electrolysis of soil in a mixture of water and ethanol
- c) Flotation
- d) Thermal treatment methods:
 - Vacuum distillation (temperatures up to 200°C)
 - Steam stripping
 - Evaporation (temperatures up to 600°C)

An evaluation of the results of laboratory experiments showed that extraction with an aqueous solution of NaOH is the most promising technique for development to a practical scale. Important criteria for choosing the extraction technique are: efficiency, technical feasibility, cost, amount and composition of waste streams. Extraction with NaOH-solution is successful because of its dispersing properties. The organic bromine compounds being largely adsorbed to the humus-like particles in the soil are removed along with these particles during extraction, resulting in decontamination of the treated soil.

Experiments on a bench scale and a pilot-plant scale were conducted to collect all relevant information for scaling-up purposes. Attention was paid to the conditions during soil extraction, apparatus suitable for the extraction process and cleaning of the polluted extracting agent. Data collected from these experiments made it possible to design an onsite treatment installation. Figure 15 shows a process scheme of the installation. The following process-steps can be distinguished:

 Soil pre-treatment to separate large objects (e.g. stones) and reduce the size of large clods of soil (crushing and wet sieving).

- 2) Intensive mixing of soil with extracting agent (approx. 0,2% NaOHsolution); the soil-to-water ratio is about 3 to 1 on a weight basis.
- 3) Extraction and washing of the soil with clean extracting agent in countercurrent flow in two modified screw classifiers in line.
- Dewatering of soil before re-deposition. The remaining alkalinity of the soil will be largely neutralised by absorption of CO₂ from the ambient air.
- 5) The overflow of the first modified screw classifier is led through a settling tank for fine mineral particles dragged out from the screw classifier by the extracting liquid. The particles that settle, with diameters between approx. 35 µm and 60 µm (approx. 1% of the total soil), are collected from time to time and washed separately by mixing . them up with NaOH-solution.
- 6) Sludge forming by adding lime as coagulant and polyelectrolyte as flocculant. The sludge formed can be separated in a tiltable plate separator.
- Dewatering of the sludge in a solid bowl centrifuge with scroll discharge.
- 8) Effluent polishing by deep bed filtration, activated-carbon adsorption and finally anion exchange to remove any bromides formed by hydrolysis. The cleaned extracting agent can be recycled to the extraction process in the screw classifiers.

The proposed process can be operated without any specific bottlenecks. Experiments showed that it is possible to remove the bromine compounds from the soil down to a level of 1 mg Br/kg or less. The cleaned extracting agent contains less than approx. 0,6 mg Br/kg, the main part of which is bromide.

The waste sludge produced contains almost all the humus-like substances, very fine mineral particles (< 30 μ m) and furthermore a high concentration of bromine compounds. The amount of sludge produced is about 5% of the total amount of contaminated soil due to the high water content of the dewatered sludge (approx. 75%). The effluent polishing step produces small amounts of spent activated carbon (approx. 1 l/ton of soil) and some regeneration liquid of the anion exchanger (approx. 13 l/ton of soil).

3.3 <u>Removal of cyanides (laboratory and pilot-plant scale</u> <u>investigations)</u>

Abandoned gaswork sites dating from the 19th and the first half of the 20th century are often contaminated with cyanides. Cyanides were generally disposed off as complexes with iron which are quite immobile (e.g. ferri-ferrocyanide). However, in some cases cleaning up can be necessary from an environmental point of view. Such a site was found in The Hague (Netherlands) in 1981.

TNO and HBG* started a study to investigate and assess alternative techniques for cleaning up the sandy soil in 1982. The techniques investigated were:

- Scrubbing to reduce the size of ferri-ferrocyanide particles, followed by washing out with water (classification);
- Flotation;
- Extraction with aqueous alkali in order to solubilize the cyanides;
- Chemical treatment with NaClO and Ca(ClO)₂ to form less harmful cyanides.

Thermal treatment was not included, for destruction of complex iron cyanides probably needs temperatures over 1800°C. Tests on a laboratory scale showed that chemical treatment is not successful and that flotation is sensitive to changes in composition of the soil.

Evaluation of the results of the experiments based on scrubbing and extraction showed that extraction is the most promising technique for development to a practical scale.

In order to assess all relevant parameters for scaling up of the extraction technique, experiments were carried out on a bench scale and a pilot-plant scale. Data collected from these experiments made it possible to design an on-site treatment installation.

TNO: Netherlands Organisation of Applied Scientific Research HBG: Hollandsche Beton Groep N.V. (Dutch Concrete Group)

Figure 16 shows a process scheme of the cleaning-up installation. The following steps can be distinguished:

- Soil pre-treatment to separate large objects (e.g. wood, stones);
- 2) Extraction with aqueous alkali in a mixing device (e.g. scrubber); the pH is approx. 11, and the soil-to-water ratio is about 2 to 1 on a weight basis;
- 3) Separation of coarse sand (e.g. settler), dewatering (dewatering screen) and, finally, neutralisation;
- 4) Separation of fine sand (hydrocyclones or flocculation followed by about four countercurrent extraction steps with aqueous alkali to remove cyanide to a sufficiently low level. Finally, the fine mineral fraction is dewatered in a solid-bowl centrifuge;
- 5) Precipitation of dissolved cyanides by pH-adjustment and addition of iron salts. The precipitate is separated (e.g. tiltable separator) and dewatered (e.g. solid-bowl centrifuge).

The most troublesome step in the process is the separation between the fine mineral fraction (approx. 30 to 65 μ m) and the extracting agent. The best results were obtained with flocculation and filtration.

Experiments showed that it is possible to remove over 99% of the cyanides present, down to levels of approximately 10 mg CN^{-}/kg or less. The cleaned water (after precipitation) contained less than 1 mg CN/kg.

The waste sludge produced contains high concentrations of cyanides and furthermore humus-like substances, clay and silt, up to approx. 40 µm. The amount of waste sludge is about 2% of the total amount of soil to be cleaned.

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3.4 <u>Removal of volatile hydrocarbons</u>

The contaminants present in the soil comprise a large variety of volatile hydrocarbons (boiling temperature < 300°C), among which are alcolhols, phenols, benzene, toluene, naphtalene, petrol, kerosine. These volatile compounds can be stripped in a thermal treatment installation.

Ecotechniek* has developed a full-scale treatment installation in which soil is heated to 200 - 300°C and the released vapours are burned at about 800°C.

In the spring of 1982, soil containing hydrocarbons from a former gas work site at Den Helder (Netherlands) was cleaned up with this installation. The following gives a brief description of the treatment installation and the results obtained.

Figure 17 presents the process scheme of the on-site installation. The following process steps can be distinguished:

- Soil pre-treatment to separate large objects and regulate the dosing rate of soil;
- 2) Heating; two-stage rotating drum evaporator. In the first stage, soil is preheated indirectly by hot gases from the afterburner (4). The soil is transported to the second drum where the soil is heated directly to 200 - 300°C by a flame;
- 3) Cooling; the hot soil is cooled with water in a mixing device;
- Afterburning; the exhaust gases from the evaporator (2) are burned with excess air at temperatures over 800°C;
- 5) Gaswashing; gas washer to separate the fine mineral particles from the gas that were dragged out from the rotating drum;
- 6) Settling; a settler is added to separate the fine mineral particles from the washwater. The settled particles can be re-deposited with the cleaned soil.

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^{*}Ecotechniek B.V., Postbus 39, 3454 ZG De Meern, Netherlands

According to Ecotechniek, the general characteristics of the process are:

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- removal of hydrocarbons with boiling points below 300°C;
- hydrocarbons with sufficiently high vapour pressures at 300°C are removed to a large extent (approx. 80 - 95%). Examples are lindane and some polycyclic aromates;
- not all organic chemicals decompose completely to harmless products in an afterburner at 800°C within a few seconds;
- the treated soil is not affected in its structure.

At Den Helder, approximately 5000 tons of soil were found to be contaminated to an appreciable extent with hydrocarbons from a former gaswork site. Regular analysis of cleaned soil showed the amounts of benzene, toluene, xylene, styrene and ethylbenzene to be always below the detection limit (0,05 mg/kg). Naphtalene however, being less volatile, was found in some soil samples to be present in concentrations of up to about 1 mg/kg and in one case even 3.3 mg/kg. Yet these values are below the maximum allowable concentration (5 mg/kg). Stack gases contained approx. 10 ppm CO, 8 ppm $C_x H_y$, 83 ppm SO₂, 51 ppm NO_x and 76 mg/m³ dust.

4. CONCLUSIONS

- For the on-site treatment of contaminated soil a large number of processes are basically available. These processes mainly originate from experiences already gathered in e.g. hazardous-waste and effluent treatment, and in ore processing and soil handling.
- 2) Although little work has yet been done on the evaluation of the different treatment principles, it can often be predicted whether certain processes promise good possibilities for application. To summarise the expected applicabilities of the different processes, these have been listed in the table. As far as possible, other valuable information has also been included in this table. It is evident that much of the information is of a rather qualitative nature, which is caused by the lack of quantitative information at this moment.
- 3) In fact, only thermal treatment and extraction procedures are in such an advanced stage of development that application will be possible in some cases at this moment. In the Netherlands, the thermal treatment of soil with the object to evaporate the contaminants and treat the exhaust gases in an afterburner is already operational.
- 4) The fact that only little information is available concerning the other modes of soil treatment does not imply that they do not offer interesting potential applicabilities. On the contrary, many principles of operation are interesting enough for more detailed investigation and further evaluation. Based on this evaluation, the most interesting alternatives should be developed to practical applications to make it possible to treat sites having different kinds of contamination profiles at reasonable costs.
- 5) The conclusion is that the development of on-site processes should be the subject of an intensive study in the near future in order to solve the numerous problems of severe soil contamination we are facing at the moment.

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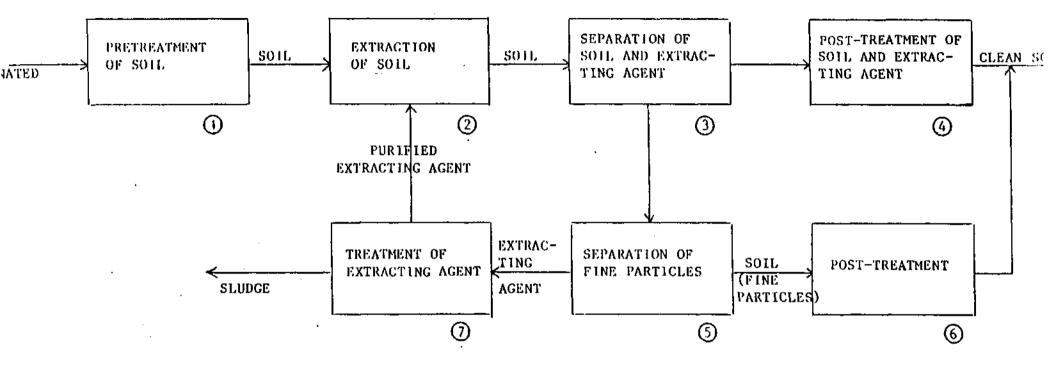
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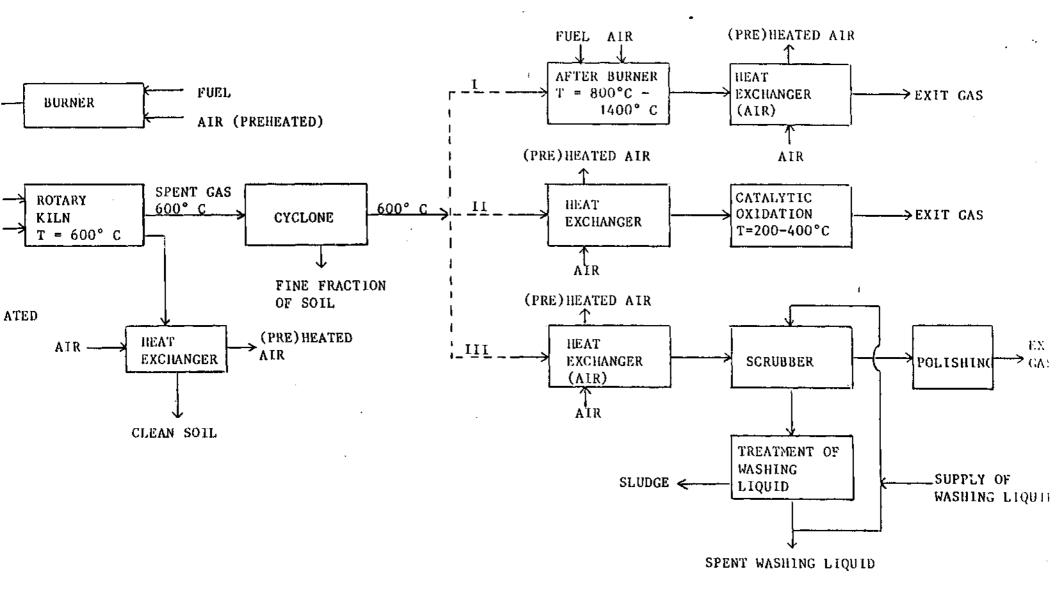
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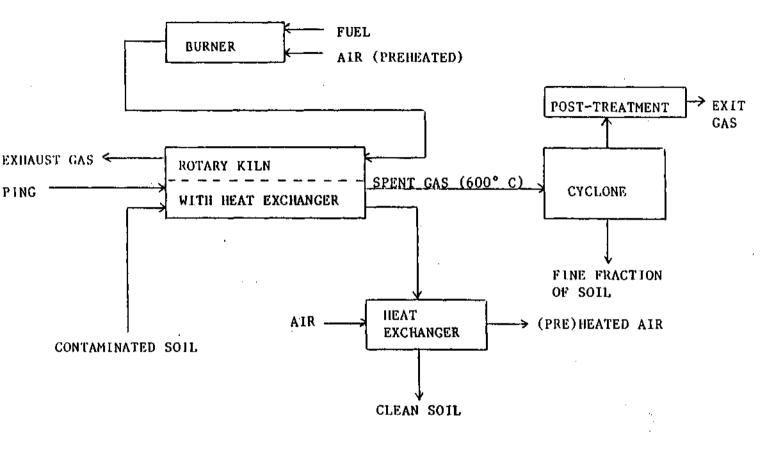
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IGURE 1 : EXTRACTION OF CONTAMINATED SOIL.

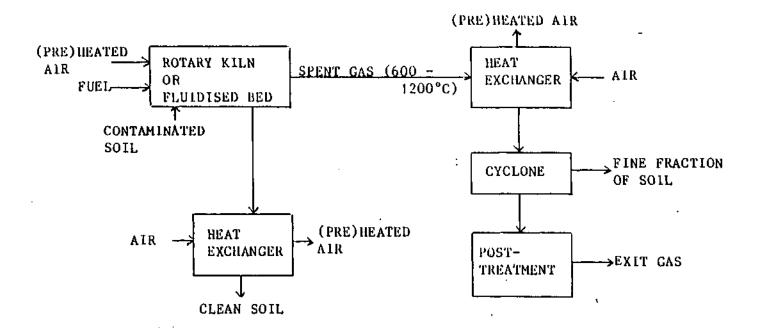
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URE 2 : THERMAL TREATMENT OF SOIL BY DIRECT HEAT TRANSFER AND EVAPORATION OF CONTAMINANTS.



GURE 3 : THERMAL TREATMENT BY INDIRECT HEAT TRANSFER AND EVAPORATION OF CONTAMINANTS.



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FIGURE 4 : THERMAL TREATMENT BY INCINERATION.

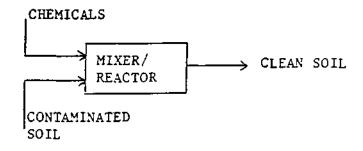


FIGURE 5 : TREATMENT OF SOIL BY MIXING UP WITH SUITABLE CHEMICALS

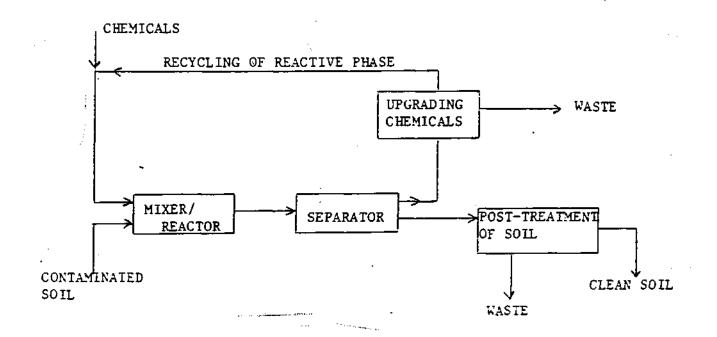


FIGURE 6 : CHEMICAL TREATMENT OF SOIL BY AN EXCESS OF REACTIVE LIQUIDS OR GASES.

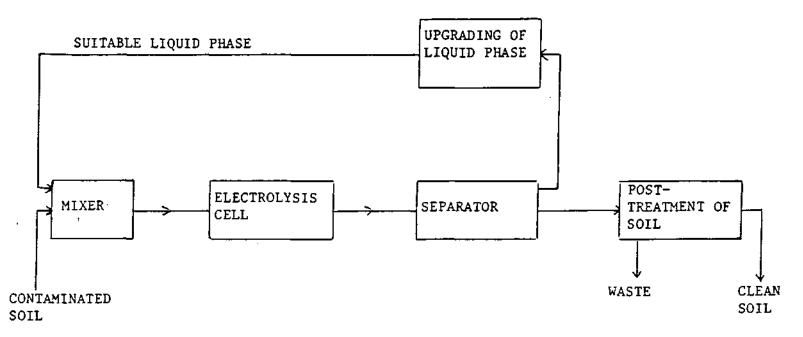


FIGURE 7 : TREATMENT OF SOIL BY ELECTROLYSIS.

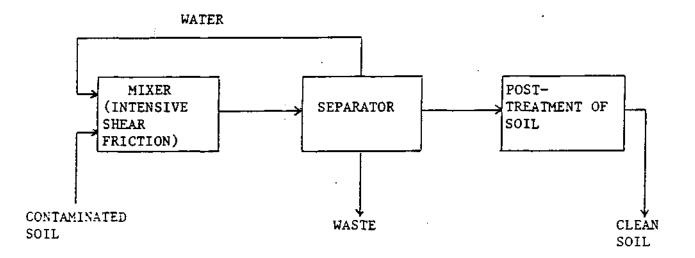


FIGURE 8 : SEPARATION BASED ON DIFFERENCES IN SPECIFIC GRAVITY.

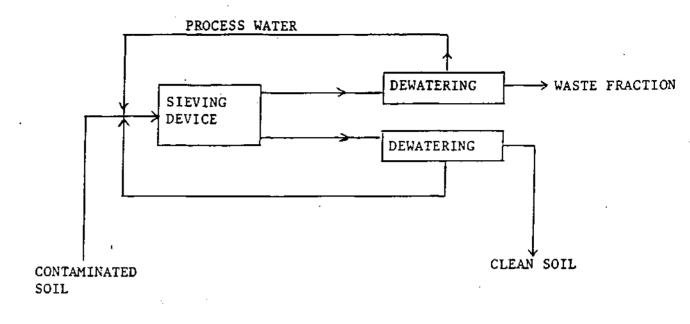


FIGURE 9 : SEPARATION BY WET SIEVING.

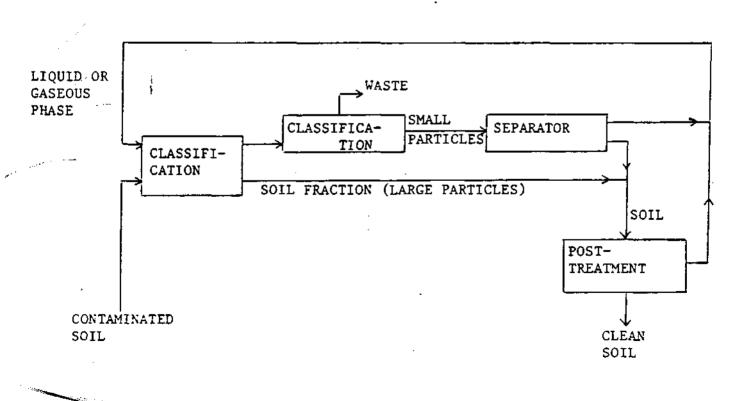


FIGURE 10 : SEPARATION BY CLASSIFICATION.

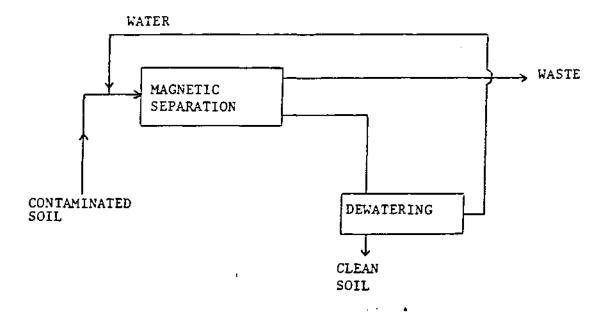


FIGURE 11 : CLEANING UP OF SOIL CONTAMINATED WITH MAGNETIC, HAZARDOUS PARTICLES.

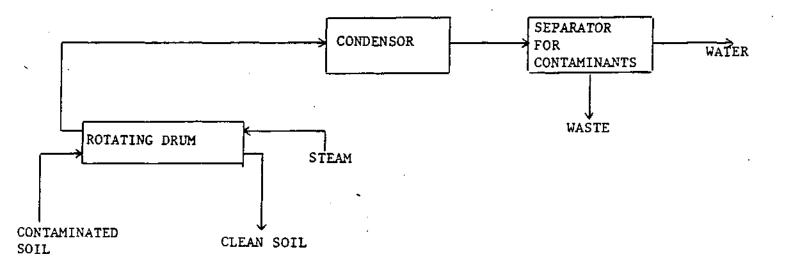


FIGURE 12 : TREATMENT OF SOIL BY STEAM STRIPPING.

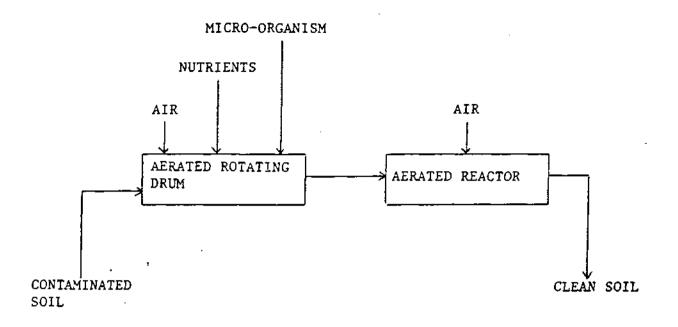


FIGURE 13 : MICRO-BIOLOGICAL TREATMENT OF SOIL.

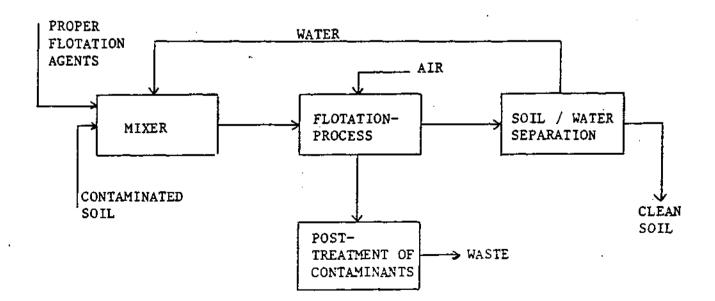


FIGURE 14 : TREATMENT OF SOIL BY FLOTATION.

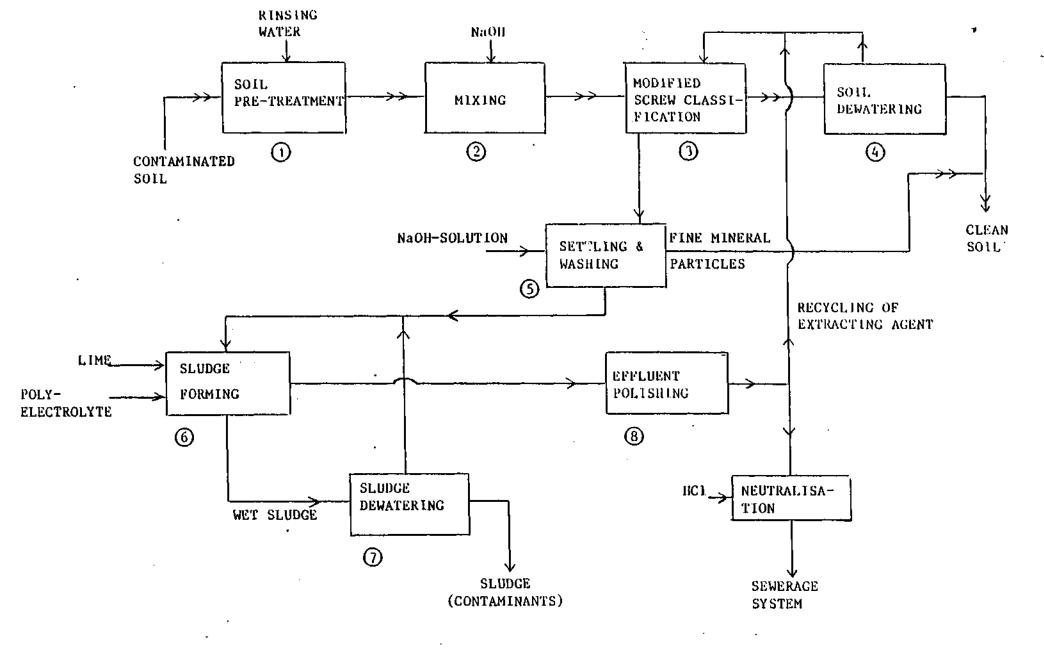


FIGURE 15 : PROCESS SCHEME OF THE PROPOSED ON-SITE TREATMENT INSTALLATION FOR REMOVING ORGANIC BROMINE COMPOUNDS.

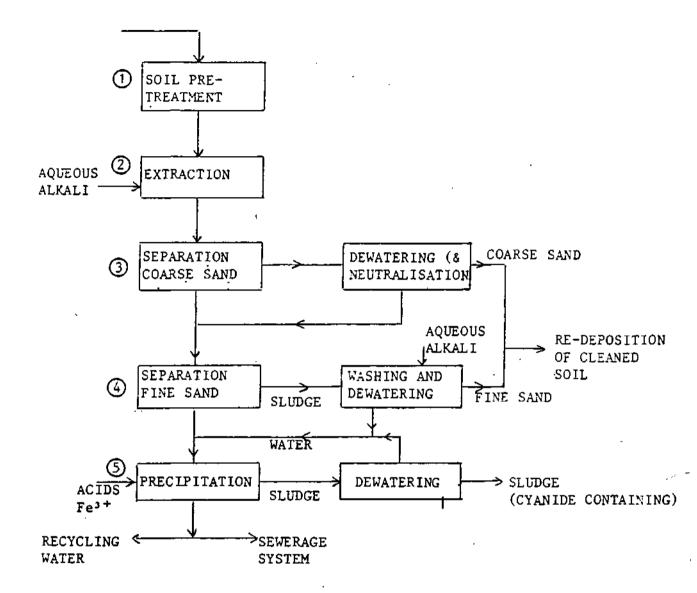


FIGURE 16 : PROCESS SCHEME OF THE PROPOSED TREATMENT INSTALLATION FOR CYANIDE REMOVAL.

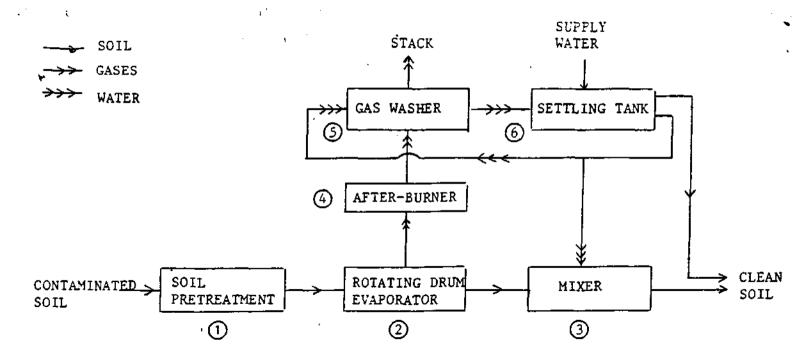


FIGURE 17 PROCESSSCHEME OF AN ON-SITE TREATMENT INSTALLATION FOR EVAPORATION OF HYDROCARBONS AND DESTRUCTION IN AN AFTER-BURNER.

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ATMENT PROCESS FOR ON-SITE LICATION	STAGE OF DEVELOP- MENTS OF THE TREATMENT PROCESS 1)	APPLICABILITY OF THE TREATMENT PROCESS 2)	ENERGY REQUIRE- MENT OF THE TREATMENT PROCESS 3)	BALANCE BETWEEN POSITIVE AND NEGATIVE FACTORS OF THE TREATMENT PROCESS 4)	4 PROSPECTS TO DEVELOP THE PRO- CESS FOR ACTUAL APPLICATION 5)
EXTRAC'I ION	0	М, Н, ШН, С	+	+	+
THERMAL TREATMENT . EVAPORATION BY DIRECT CONTACT WITH HEATED GAS - AFTER-BURNING OF GASES	÷	н, ин	_	+/0	+
- CATALYTIC AFTER-BURNING	•			+/0 1	
OF GASES - WET SCRUBBING	-	н, нн н, нн	-	0	0/-+/0
. EVAPORATION OR INDIRECT CONTACT WITH HEATED GAS - AFTER-BURNING OF GASES - CATALYTIC AFTER-BURNING - WET SCRUBBING	- -	н, нн н, нн н, нн н, нн	 	+/0 +/0 +	+ 0 +
. INCINERATION - AFTER-BURNING OF GASES - CATALYTIC AFTER-BURNING - WET SCRUBBING	-	н, нн (С) н, нн (С) н, нн (С) (м)	- - ·	0 0 0	+ 0/- +/0
CHEMICAL TREATMENT	-	н, ни, с, м	0	+	+/0
PHASE SEPARATION	· · ·	н, нн, (с) (м)	+	+/0	+/0
STEAM STRIPPING	-	н, нн	0	0	0
BIOLOGICAL TREATMENT		н, інн (С)	+	0	0
FLOTATION	0/-	н, шн, с, м	+	0	+/0
GCRIPTS: SEE NEXT PAGE					

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SUBSCRIPT TO TABLE

1)

- : NOT INVESTIGATED OR ONLY ON A LABORATORY SCALE.

0 : INVESTIGATED ON A PILOT PLANT SCALE.

+ : APPLIED ON-SITE IN ACTUAL CASE OF CLEANING UP.

2)

- M : HEAVY METALS
- H : HYDROCARBON'S
- HH : HALOGENATED HYDROCARBONS
- C : CYANIDES

3)

- + : LOW ENERGY NEED
- 0 : MODERATE ENERGY NEED
- : HIGH ENERGY NEED

4)

POSITIVE FACTORS : . LARGE APPLICABILITY, WITH RESPECT TO NUMBER OF CONTAMINANTS

- . LOW ENERGY NEED
- . FEW BOTTLENECKS TO BE SOLVED
- . LOW AMOUNT OF RESIDUAL WASTE
- . LOW INVESTMENT COSTS
- . UNIVERSAL APPLICABILITY, WITH RESPECT TO NUMBER OF SITES
- + : POSITIVE BALANCE
- 0 : POSITIVE AND NEGATIVE FACTORS ARE ABOUT EQUAL
- : NEGATIVE BALANCE

5)

+ : GOOD

- 0 : MODERATE
- : POOR