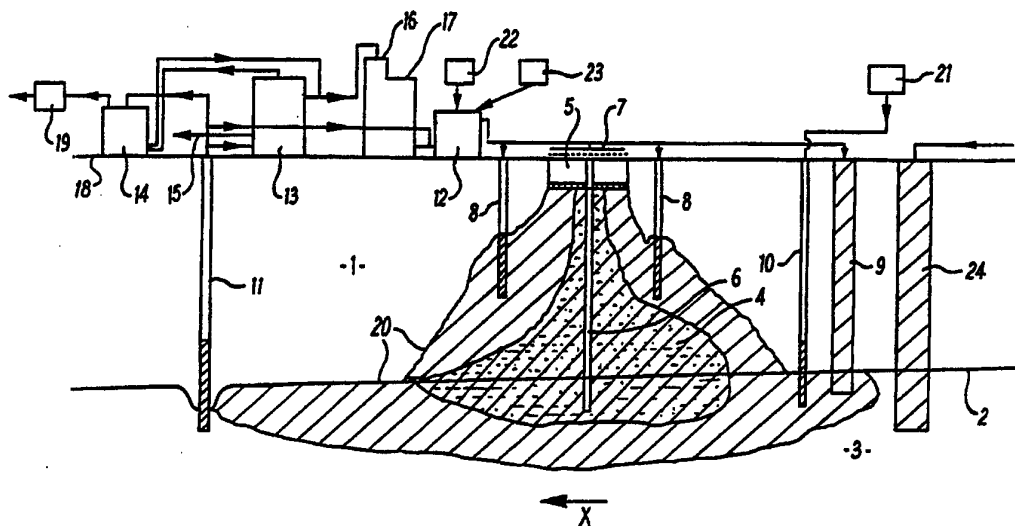




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(54) Title: PROCESS FOR THE TREATMENT OF CONTAMINATED LAND



(57) Abstract

A process for the treatment of metal species contaminated land or soil which includes the steps of treating the land or soil to convert the metal species into metal sulphate and thereafter treating the land or soil to convert the metal sulphate contained therein by a biochemical process to convert the same to insoluble metal sulphide.

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Process for the treatment of contaminated land

The present invention relates to a process for the treatment of contaminated land, in particular a biochemical process for the immobilisation of contaminants, especially heavy metal, contaminants within land or soil.

World-wide, substantial amounts of land have been contaminated with both organic and inorganic compounds as a result of industrial, waste disposal and other activities. Examples of such contaminants include: toxic heavy metals including mercury, cadmium, barium and lead, radionuclides such as actinides and fission products and organic pollutants such as polychlorinated biphenyls (PCBs), dioxins, coal tars and trichloroethylene. Such contaminants can pose a significant threat to ground water and therefore drinking water supplies and in many cases either limit, or prevent land re-use. Additionally, as a result of recent legislation in the United States of America and likely similar legislation within the European Community and elsewhere, waste producers are becoming increasingly liable to prosecution and to meet the costs of recovery and clean up if they do not act responsibly towards their wastes. Consequently there is a growing need for technologies which can solve the problem of contaminated land.

To date, a number of techniques have been developed to remediate contaminated land. Examples include: soil stabilisation, electromigration, vitrification, volatilisation, incineration, soil washing, pump and treat systems, land farming, slurry phase bioremediation etc. Many of these known techniques possess several limitations including:

- a) Unsuitability to treat metal contaminated land, eg as in the case of biological pump and treat system;
- b) the generation of secondary wastes which are difficult to control and handle and/or are of high

volume, eg as in the case of soil stabilisation and incineration;

c) unsuitability for treating land in-situ, eg many soil washing and stabilisation systems require soil excavation and pre-treatment prior to on-site backfilling;

d) unsuitability for treatment of a range of different sites; eg the efficiency of metal removal using electrokinetic techniques can be limited by the presence of precipitated salts or secondary minerals; the efficiency of soil stabilisation techniques is limited by the presence of organics;

e) high costs, eg as in the case of landfilling, incineration, vitrification and electrokinetics.

The purpose of the present invention is to provide a process for the treatment of contaminated land showing a minimum of the aforementioned limitations.

According to the present invention there is provided a process for the treatment of metal species contaminated land or soil which includes the steps of treating the land or soil to convert the metal species into metal sulphate and thereafter treating the land or soil to convert biochemically the metal sulphate contained therein to insoluble metal sulphide. Other metal salts contained in the soil or land may be similarly reduced.

The metal species to metal sulphate conversion may be brought about by a process in which the land or soil is contacted with a solution of sulphuric acid or metal sulphate. Alternatively, the land or soil may be bioleached by causing a source of sulphurous material either in the soil or in an external bioreactor to form sulphuric acid by a biochemical route, eg in the manner described below. The sulphuric acid so formed thereby produces dissolution of the metal species contaminants.

Several metal species may be present in the land or soil and these may be converted to various metal sulphates

together. The term "metal species" as used herein includes metals, alloys, metal salts, metalloids, and metal containing compounds and complexes.

The present invention therefore beneficially provides a process for mineralising metals (particularly heavy metals) possessing insoluble sulphides in-situ within contaminated land. The process is compatible with existing biochemical processes for degrading organic contaminants and for treating metal contaminated land, eg the cyclic remediation processes as described in Applicants' copending GB 9414426.8 and GB 9414425.0 (both the subject of copending PCT applications filed on even date herewith). The present process is particularly applicable for:

1. Metals possessing sulphates which are insoluble and thus not amenable to bioleaching, or sulphuric acid washing to remove the metals, eg lead and barium.
2. Where metal contamination has occurred substantially below the surface and is thus not readily amenable to ex-situ techniques, eg contamination from underground storage tanks.
3. As a close-down procedure following in-situ bioleaching in a cyclic a bioremediation process as described in GB 9414426.8 and GB 9414425.0. This prevents any remaining metals entering ground water following the remediation.
4. Where the contamination is present in an anaerobic zone, or an area which can be maintained anaerobic and will thus not be subject to treatment by leaching.
5. Where the treatment will reduce metal concentrations entering ground water aquifers to acceptable limits.
6. Where the treatment will allow the contaminants to be moved to a greater depth in the land and thereby pose less risk.

This invention involves in the sulphate to sulphide conversion step stimulating naturally occurring or added sulphate reducing bacteria within the contaminated area, to convert aqueous metal sulphates to insoluble metal sulphides either directly or through the action of hydrogen sulphide. Micro-organisms capable of this transformation include: species of *Desulfovibrio*, *Desulfomonas* and *Desulfotomaculum*. These organisms oxidise simple organic compounds such as lactate and ethanol whilst simultaneously reducing sulphates to sulphides, to derive the energy necessary for their growth. However, more complex carbon sources can occasionally be used, eg phenolic compounds, or organic materials within the soil.

As sulphate reducing bacteria (SRB) require anaerobic environments for their growth, ie a redox potential of $<-100\text{mv}$, and occur naturally within anaerobic soil environments, they are ideally suited to use in the sulphate conversion step. Additionally, avoidance of the necessity to supply oxygen overcomes one of the major limitations of many existing in-situ bioremediation processes.

Besides a requirement for an organic electron donor, sources of one or more various nutrient additives are desirably added to SRB to promote their growth and activity; such additives include one or more of: sulphate, phosphate, ammonium and possibly magnesium sulphate or calcium chloride as determined by the particular site. One or more of these ingredients can be injected into the contaminated area using existing methods.

To avoid the release of any nutrients or solubilised metals into ground water supplies, the process may also incorporate a leachate recovery system. Thus, leachate may be drained, collected and separated from the soil. Insoluble sulphides may be allowed to remain in the soil

as they present a reduced danger of contamination of nearby water supplies.

The metal species contaminants in the land to be treated by the process according to the present invention may be contained on the surface of the particulate material of the land or may be bound inside the particles thereof.

The said metal of the metal species contaminants may include:

- i) actinides or their radioactive decay products or compounds thereof;
- ii) fission products;
- iii) heavy metals or compounds thereof.

Actinides are elements having periodic numbers in the inclusive range 89 to 104.

The term 'fission product' as used herein refers to those elements formed as direct products (or so-called 'fission fragments') in the fission of nuclear fuel and products formed from such direct products by beta decay or internal transitions. Fission products include elements in the range from selenium to cerium in the Periodic Table including elements such as ^{56}Ba , ^{40}Zr and ^{52}Te ^{55}Cs and ^{58}Ce .

Non-radioactive heavy metals which may be contaminants of land to be treated by the process of the present invention include toxic metals such as nickel, lead, cadmium, barium and mercury which are commonly found as earth contaminants or in aquatic sediments near industrial plants which have employed chemicals containing those elements and on waste disposal sites.

The metallic species contaminants immobilised in the process of the present invention may include a mixture of radioactive and non-radioactive metallic species contaminants.

In application of the process according to the present invention, a suitable mixture of an aqueous solution and a

source of sulphurous material bioconvertible into sulphuric acid may be injected into or mixed with the soil or land to be treated in order to bring about the conversion to metal sulphates. Other ingredients such as nitrogen-rich or phosphorus-rich materials and air may optionally be added. The bioconversion to sulphates may be carried out in a known way by microbial agents present in the land. These agents may be naturally present or may be added to the land. The sulphurous material may comprise either elemental sulphur or another reduced form of sulphur preferably injected in aqueous medium.

As an alternative, the sulphuric acid in each of the above examples may be produced chemically or biochemically in a separate bioreactor and added to the land or soil material after production.

The formation of metal sulphates may also be induced by addition of other metal sulphates, eg sodium sulphate, to react with the contaminant metals.

Bioconversion to produce sulphate ions carried out in the soil to be treated may be brought about by the known action of naturally occurring sulphur oxidising organisms including: *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*. These organisms obtain the energy necessary for their growth by the oxidation of reduced forms of sulphur to metal sulphates and sulphuric acid, or by the oxidation of ferrous iron to ferric iron. In addition to acid leaching mentioned above metal release can occur by one or more of the following mechanisms:

- a) direct attack of metal sulphides;
- b) by electrochemical processes (Galvanic conversion), resulting from contact between two dissimilar metal species immersed in a suitable electrolyte, eg sulphuric acid; or
- c) by the oxidative effect of ferric sulphate.

The acid used for metal sulphate production within the soil may be produced by the growth of a consortium of

naturally occurring sulphur oxidising organisms, eg Thiobacilli. If the soil is deficient in the appropriate micro-organisms, then these micro-organisms may be added as a mixed consortium obtained from similar soil environments.

In a particular example of the present invention the in-situ conversion (reduction) of sulphates to sulphides may be carried out following a cyclic process treatment of the contaminated land as described in Applicants' 9414426.8 or 9414425.0. In both cases, metal species in the contaminated land are bioleached as sulphates, the sulphates are reduced to sulphides in a separate bioreactor, and H_2S and soluble sulphides are separated from insoluble sulphides and converted to a re-usable form of sulphurous material for re-use in the bioleaching step. The in-situ reduction of sulphates may be carried out following the bioleaching of metals susceptible to be solubilised as metal sulphates (or other soluble salts), ie at the end of the cyclic process. The land which has been treated by bioleaching may be treated by adding cultures of an appropriate biomass to provide the required SRBs for in-situ sulphide production. The biomass may be the same as that employed in the bioreactor in the cyclic phases of the process. In fact, the biomass applied to the land may be that which has been earlier employed in the bioreactor to provide sulphide production during the cyclic phases.

Embodiments of the present invention will now be described by way of example with reference to the accompanying drawing, in which:

Figure 1 is a diagrammatic cross-sectional view of a region of land being treated in-situ by a process embodying the present invention together with equipment used in the process.

As shown in Figure 1, a region of land is to be treated initially by a cyclic decontamination process

followed by an in-situ mineralisation step to complete remediation. The region comprises a layer 1 of soil overlying an underground aquifer 3 below a level 2. The layer 1 incorporates a metal contaminated region 4 which has been produced by migration of contaminants from a waste sump 5 provided in the surface of the layer 1. The region 4 extends into the aquifer 3. A monitoring well 6 projects downward through the region 4 to enable measurements on the extent of contamination in the region 4 to be determined. The depth and dimensions of the contaminated region 4 have previously been determined using appropriate known analytical techniques. Ground level is indicated by numeral 18.

Nutrients from a nutrient source 22 and acid which may be carried in a suitable carrier liquid, eg aerated water, are applied to the base of the empty sump 5. This application is carried out by a sprayer 7. This liquid is also applied via appropriately positioned injection wells 8 and through an infiltration gallery 9, so as to permeate through the material in the contaminated region and promote soil acidification. Elemental sulphur may also be added to and mixed into areas of shallow contamination such as the base of the sump 5 further to promote in-situ bioleaching.

In order to enable aerobic conditions to be developed and maintained within the contaminated region 4 air is blown by an air blower 21 attached to a series of vent wells 10, (one of which is shown) either to draw air through the contaminated region 4 in the layer 1 or to inject air into the ground water in the aquifer 3 or both. Additionally, the rate of nutrient addition may be varied to avoid the creation of anaerobic conditions within the contaminated region 4. The plume or region in the layer 1 and aquifer 3 supplied with nutrients and acid is indicated by reference 20. This plume encompasses the contaminated region 4 in the layer 1 and aquifer 3.

This treatment produces acid metal leaching in the region 4 in the manner described above. This may continue over weeks or months until the soil in the contaminated region 4 is substantially free of contaminating metals as determined from time-to-time by suitable analysis.

The products of the metal leaching treatment are collected within a portion of the aquifer 3, either naturally occurring or artificially created in a direction X, and are received by and returned to the surface above the layer 1 via a series of recovery wells 11 (one shown) using appropriate pumps (not shown). The level 2 of the aquifer 3 may be adjusted by addition of water through an infiltration gallery 24 to assist water flow in the direction X.

The collected liquor is then delivered to a selected one of:

(a) a buffer tank 12 for aeration and addition of appropriate nutrients before re-application to the contaminated area. This is the principal route during initial operation of the process;

(b) a bioprecipitation reactor 13;

(c) a gas liquid contactor 14 to scrub hydrogen sulphide from the gaseous effluent from bioprecipitation.

Liquor enters the reactor 13 at its base and flows upward through the reactor 13. As it does so, sulphate reducing organisms present in the reactor 13 convert the influent sulphates to sulphides in the manner described above.

The gaseous effluent produced during bioprecipitation in the reactor 13 is passed through the gas liquid contactor 14 connected to the reactor 13. The contactor 14 permits hydrogen sulphide recovery. The gas stream leaving the contactor 14 is passed through a secondary scrubber unit 19 and discharged to atmosphere.

Bioprecipitated sludge containing insoluble sulphides is collected in the base of the reactor 13 and transferred

via a pipeline 15 to a separate treatment process, eg biologically enhanced metal fixation or is dewatered and collected and delivered to another site for metal recovery. The liquor obtained by dewatering the sludge may either be returned for re-use in the bioleaching process, or further treated and discharged.

The effluent liquor containing dissolved sulphides arising from bioprecipitation is extracted and combined with the aqueous sulphide stream arising from the gas/liquid contactor 14. The combined aqueous sulphide stream is then pumped through a gas/liquid contactor 16 and into a sulphide oxidation reactor 17. Contactor 16 ensures that any gaseous hydrogen sulphide released by acid in the reactor 17 is re-dissolved by the alkaline influent liquor.

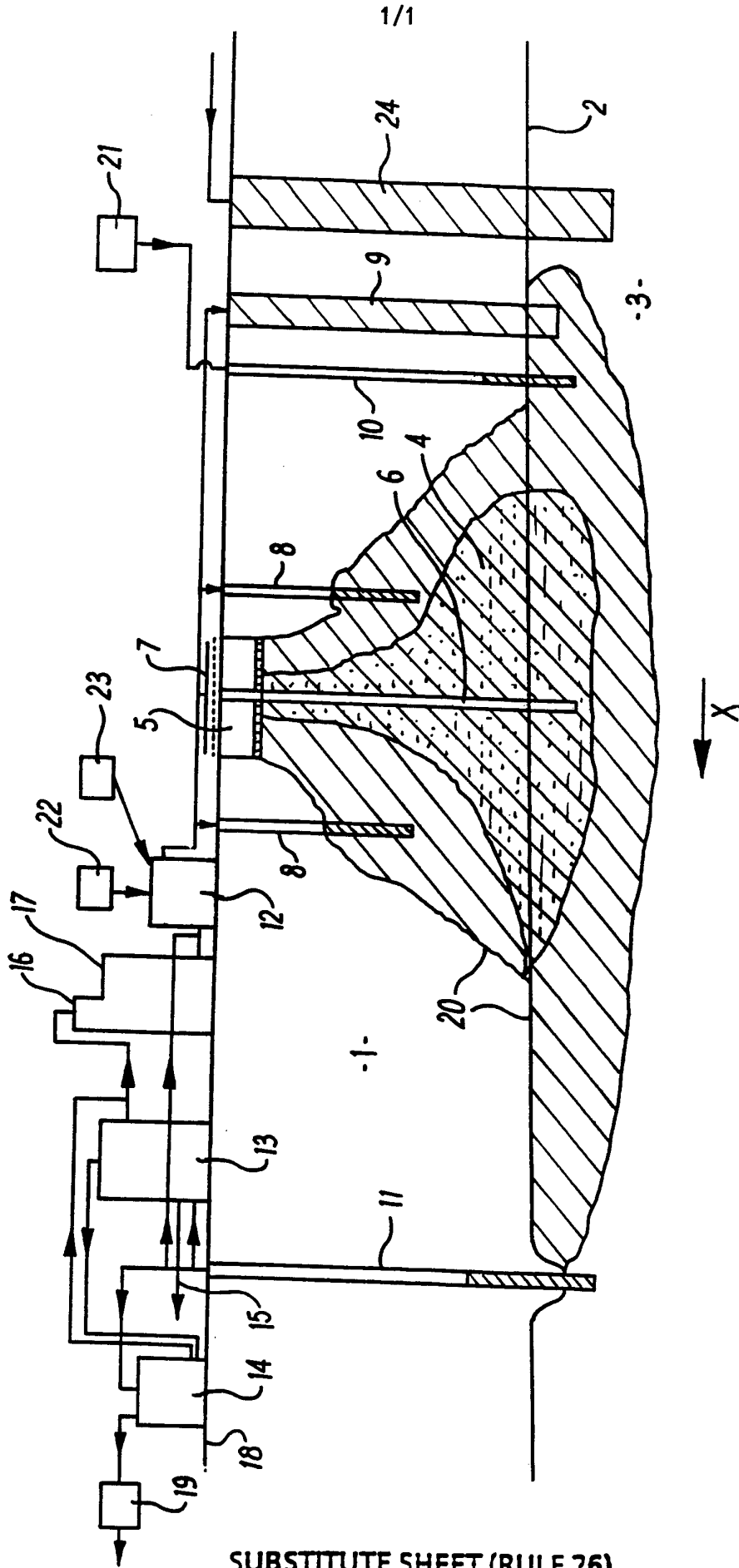
Within the oxidation reactor 17, the sulphide containing liquor is intimately mixed with suitable micro-organisms and oxidised to sulphate in the manner described above. The acid liquor produced is then transferred to the buffer tank or bioreactor 12 where further elemental sulphur may be added from a sulphur source 23 if required, and oxidised to sulphuric acid, by micro-organisms carried over from reactor 17 before re-addition to the contaminated material in the soil 1 in the manner described above (via the wells 8 and gallery 9 and sprayer 7).

The metal removal treatment process is therefore cyclical and metal contaminants in the portion 3 of the soil layer 1 are, during various cycles of the metal removal process, gradually leached by the leachate solution containing biochemically formed sulphuric acid and recovered as an insoluble sulphide formed in the bioprecipitation reactor 13. A proportion of the sulphur is recovered by oxidation of sulphides in the oxidation reactor 17 and is re-used in the soil acid leaching of metal contaminants.

Following the cyclic part of the process, biomass which has been used in the bioreactor 13 is transferred to be added in aqueous form to the soil 1 via the wells 8, gallery 9 and sprayer 7. Metals remaining in the soil 1 which have not been removed by bioleaching during the cyclic part of the process are thereby gradually converted to insoluble sulphides and fixed in the soil thereby eliminating any problems caused by subsequent slow leaching over a period of time. Further additions of the biomass, water and other nutrients suitable to promote the known reduction step may be made from time-to-time. The composition of samples of the soil may be analysed at suitable intervals until suitable in-situ bioconversion to insoluble sulphides has been achieved.

CLAIMS

1. A process for the treatment of metal species contaminated land or soil which includes the steps of treating the land or soil to convert the metal species into metal sulphate and thereafter treating the land or soil to convert the metal sulphate contained therein by a biochemical process to convert the same to insoluble metal sulphide.
2. A process as in Claim 1 and wherein the metal sulphate conversion is brought about by a leaching process in which the land or soil is contacted with a sulphuric acid wash.
3. A process as in Claim 1 and wherein the land or soil is bioleached by causing a source of sulphurous material in the soil to form sulphuric acid by a biochemical route, the sulphuric acid so formed producing dissolution of the metal contaminants.
4. A process as in Claim 3 and wherein the bioleaching is carried out as part of a cyclic treatment process in which bioleached sulphate is reduced in a separate bioreactor to hydrogen and metal sulphides and the hydrogen sulphide is separated from insoluble sulphides and oxidised to form a re-usable sulphur source.
5. A process as in Claim 4 and wherein the land or soil is treated to provide in-situ sulphate to sulphide conversion after the bioleaching of the cyclic treatment process.
6. A process as in Claim 5 and wherein biomass substantially the same as that which has been used to provide reduction in the said bioreactor is added to the land or soil to promote in-situ sulphate reduction in the land or soil.



INTERNATIONAL SEARCH REPORT

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CLASSIFICATION OF SUBJECT MATTER		
IPC 6 B09C1/10	B09C1/02	C02F3/34 A62D3/00 C22B3/00
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 6 B09C C02F A62D C22B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE,A,41 17 515 (NOELL GMBH) 17 December 1992	1,2
A	see column 1, line 3 - line 14 see column 5; example 2 see claims 1,3-5	4
Y	---	
Y	US,A,4 108 722 (D. STOVER) 22 August 1978	1,2
A	see claims	5
A	---	
A	DATABASE WPI Week 8916 Derwent Publications Ltd., London, GB; AN 89-119928 & JP,A,01 067 299 (NAKAYAMA) , 13 March 1989 see abstract	1,3

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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
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Date of the actual completion of the international search	Date of mailing of the international search report	
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Inter national Application No

PCT/GB 95/00286

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