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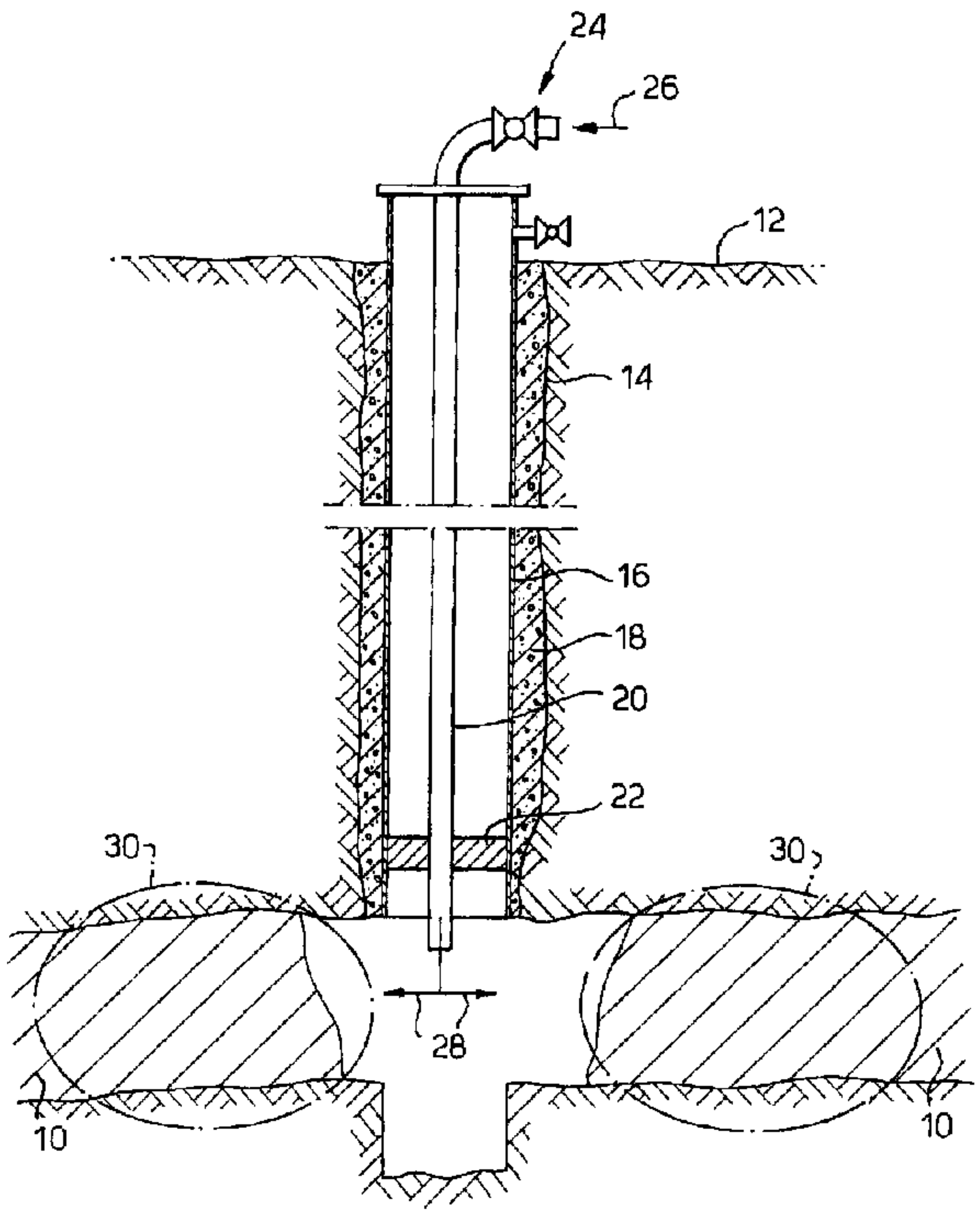
(54) Titre : STIMULATION PAR VOIE CHIMIQUE DES FORMATIONS CARBONEES SOUTERRAINES AVEC DES SOLUTIONS OXYDANTES AQUEUSES

(54) Title: CHEMICALLY INDUCED STIMULATION OF SUBTERRANEAN CARBONACEOUS FORMATIONS WITH AQUEOUS OXIDIZING SOLUTIONS



(57) Abrégé/Abstract:
A method for increasing the production of methane from a subterranean carbonaceous formation by chemically stimulating the formation of additional free surface area or cleats in the organic constituents of the formation and by causing inorganically adsorbed methane to be released from contained clay-minerals to increase the rate of methane desorption from the formation by injecting an aqueous oxidizing solution containing at least one oxidant into the formation, and thereafter producing methane from the formation at an increased rate. Suitable oxidants include peroxide, ozone, oxygen, chlorine dioxide, sodium hypochloride, water soluble salts of hypochlorous acid, perchlorate, chlorate, persulfate, perborate, percarbonate, permanganate, nitrate and combinations thereof.

Abstract of the Invention

A method for increasing the production of methane from a subterranean carbonaceous formation by chemically stimulating the formation of additional free surface area or cleats in the organic constituents of the formation and by causing inorganically adsorbed methane to be released from contained clay-minerals to increase the rate of methane desorption from the formation by injecting an aqueous oxidizing solution containing at least one oxidant into the formation, and thereafter producing methane from the formation at an increased rate. Suitable oxidants include peroxide, ozone, oxygen, chlorine dioxide, sodium hypochloride, water soluble salts of hypochlorous acid, perchlorate, chlorate, persulfate, perborate, percarbonate, permanganate, nitrate and combinations thereof.

CHEMICALLY INDUCED STIMULATIONS OF SUBTERRANEAN CARBONACEOUS FORMATIONS WITH AQUEOUS OXIDIZING SOLUTIONS

This invention relates to methods for increasing the rate of production of methane from a subterranean carbonaceous formation by chemically stimulating the formation with an aqueous oxidizing solution to increase the production rate of methane from the formation. The invention is applicable to the enhanced recovery of methane from formations consisting of carbonaceous materials deposited with inorganic materials, such as occur in carbonaceous shale formations. The increased production rate is accomplished by increasing the surface areas of the contained organic material fragments, which contain hydrocarbons, by inducing the formation of cleats and other new surfaces in these carbonaceous materials, thereby facilitating the desorbtion of light hydrocarbons from these carbonaceous formations. Carbonaceous formations such as shales, are composed in part of clay minerals. The invention is also applicable to the enhanced recovery of light hydrocarbons which are adsorbed to these clay minerals.

Substantial quantities of methane gas are found in formations containing carbonaceous materials, which may include macerals, kerogens, and other organic materials and which are present with inorganic materials such as sands, clays and like clastic materials in the formation. Such formations are referred to herein as "carbonaceous formations". Many such carbonaceous formations contain large quantities of methane, or other absorbed or adsorbed light hydrocarbons such as methane, but the methane is not readily recovered from such formations because the permeability and exposed surface area of the contained carbonaceous materials are too low to permit the efficient release of methane from the formation. The terms "absorbed" and "adsorbed" are used interchangeably in the discussion herein to refer to methane or other light hydrocarbons which are retained in or on the surfaces of the carbonaceous materials and the methane or other light hydrocarbons which are retained in or on the surfaces of the clay-mineral materials which are present in the carbonaceous formations.

Accordingly, continuing efforts have been directed to the development of methods for replicating the effects of the conditions which formed the better developed cleat systems in coal formations and increasing the production rate of methane from carbonaceous formations.

Summary of the Invention

According to the present invention, there is provided a method of increasing the rate of production of methane from a subterranean carbonaceous formation penetrated by at least one well, the method comprising:

a) injecting an aqueous oxidizing solution containing at least one oxidant selected from the group consisting of peroxide, ozone, oxygen, chlorine dioxide, hypochlorite, water-soluble metallic salts of hypochlorous acid, perchlorate, chlorate, persulfate, percarbonate, permanganate, nitrate and combinations thereof into the formation;

b) maintaining the aqueous oxidizing solution in the formation for a selected time; and

c) producing methane from the formation at an increased rate.

The injection of the aqueous oxidizing solution into the formation, and the maintenance of the solution in the formation for a selected period of time stimulates and facilitates the desorbtion of methane and other light hydrocarbons from the clay-mineral constituents of the formation; allows the methane to migrate from the formation into the wellbore; and allows the methane to be produced from the formation at an increased rate.

Some suitable oxidants are peroxide, ozone, oxygen, chlorine dioxide, hypochlorite, water soluble metallic salts of hypochlorous acid, perchlorate, chlorate, persulfate, perborate, percarbonate, permanganate, nitrate and combinations thereof.

In one embodiment of the invention, the rate of production of methane from a subterranean carbonaceous formation penetrated by at least one injection well and at least one production well is increased by:

a) Injecting an aqueous oxidizing solution containing at least one oxidant into the formation through the injection well; and

b) Producing methane from the formation through the production well at an increased rate.

The present invention is effective to enhance methane recovery from carbonaceous materials disposed with inorganic materials and enhances the recovery of methane from the inorganic materials to which and in which it is adsorbed.

The invention will now be described in greater detail with reference to preferred embodiments thereof and with the aid of the accompanying drawings in which:

FIG. 1 is a schematic diagram of a formed well penetrating a subterranean carbonaceous formation from the surface, wherein the inventive method as described may be employed.

FIG. 2 is a schematic diagram of a formed well penetrating a subterranean carbonaceous formation from the surface wherein the carbonaceous formation has been fractured and wherein the inventive method as described may be employed.

FIG. 3 is a schematic diagram of a formed injection well and production well penetrating a subterranean carbonaceous formation from the surface and wherein the inventive method as described may be employed.

FIG. 4 is a schematic diagram of a formed injection well and a production well penetrating a subterranean carbonaceous formation from the surface wherein the carbonaceous formation has been fractured from the injection well and wherein the inventive method as described may be employed.

FIG. 5 is a schematic layout of a 5-spot injection and production well pattern.

Description of Preferred Embodiments

In the discussion of the Figures, the same numbers will be used throughout the specification to refer to the same or similar components.

In Fig. 1, a carbonaceous formation 10 penetrated from a surface 12 by a wellbore 14 is shown. The wellbore 14 includes a casing 16 positioned in the wellbore 14 by cement 18. While wellbore 14 is shown as a cased wellbore it should be understood that in the preferred embodiments shown in the Figures, cased or uncased wellbores could be used. Alternatively, the casing 16 could be extended into or through carbonaceous formation 10 with perforations through the casing in the carbonaceous formation 10 providing fluid communication between carbonaceous formation 10 and wellbore 14. Wellbore 14 extends into carbonaceous formation 10 and includes a tubing 20 and a packer 22. Packer 22 is positioned to prevent flow between the outer diameter of tubing 20 and the inner diameter of casing 16. Wellbore 14 also includes equipment 24 adapted to inject a gaseous or liquid stream into carbonaceous formation 10 or to recover a gaseous or liquid stream from carbonaceous formation 10.

In the practice of the present invention, an aqueous oxidizing solution containing at least one oxidant is injected as shown by an arrow 26 through tubing 20 into carbonaceous formation 10 as shown by arrows 28. The zones treated are shown by circles 30. The aqueous oxidizing solution is injected into carbonaceous formation 10 for a selected time to enhance or stimulate the formation of additional surface area or cleats in the organic materials contained in carbonaceous formation 10. The aqueous oxidizing solution is injected for a period of time and in a quantity considered sufficient to increase the ability of the organic materials present in carbonaceous formation 10 in the zones 30 to desorb the methane and other light hydrocarbons which are absorbed on and in the organic materials. After a selected period or after a selected amount of the aqueous oxidizing solution has been injected, the well is shut in for a period of time which may be up to or greater than 24 hours. Typically, the well is shut-in until the pressure in the wellbore returns to the formation pressure and thereafter for at least 12 additional hours. Alternatively, a sufficient period of oxidizing solution presence in carbonaceous formation 10 may have elapsed during the injection of the aqueous oxidizing solution. The shut-in period allows for migration of the oxidizing solution into carbonaceous formation 10 to oxidize components of carbonaceous formation 10; thereby increasing the surface area of, and cleats in, the organic materials present in carbonaceous formation 10. The shut-in period also allows for migration of the oxidant solution into carbonaceous formation 10 to separate methane and other light hydrocarbons which are adsorbed to the clay-minerals present in carbonaceous formation 10. Subsequent to the shut-in period, water, methane or both may be recovered from carbonaceous formation 10 to de-water carbonaceous formation 10 in the zones 30 and produce methane. The term "de-water" as used herein does not refer to the complete removal of water from carbonaceous formation 10, but rather to the removal of sufficient water from carbonaceous formation 10 to open passage ways in carbonaceous formation 10 so that methane can be produced through the passage ways from carbonaceous formation 10.

The aqueous oxidizing solution contains an oxidant selected from the group consisting of peroxide, ozone, oxygen, chlorine dioxide, hypochlorite, water-soluble metallic salts of hypochlorous acid, perchlorate, chlorate, persulfate, perborate, percarbonate, permanganate, nitrate and combinations thereof. Preferred metallic salts are sodium and potassium salts. Typically, the oxidant is used in concentrations up to the solubility limit of the oxidant in the aqueous oxidizing solution. With peroxide and ozone the oxidant is typically present in amounts up to about ten (10) weight percent of the aqueous oxidizing solution, although higher concentrations can be used if desired. Such oxidants have been used previously as a fracturing fluid gel breaker in hydrocarbon-bearing formation fracturing applications and are commercially available. The injection of the oxidizing solution facilitates the formation of additional free surface area and cleats in the carbonaceous formation and facilitates the release of methane and other light hydrocarbons from the organic materials and from the surfaces of the clay-minerals to which they are adsorbed.

In the embodiments shown in Fig. 1, a single well is used for injection of the aqueous oxidizing solution to chemically enhance or stimulate the formation of additional free surface area and cleats in the organic materials present in carbonaceous formation 10 and facilitate the release of hydrocarbons adsorbed on clay-minerals present in zones 30, to result in the release of formation water and an increase in the methane production rate from carbonaceous formation 10. The term "increase" as used herein refers to a change relative to the untreated carbonaceous formation.

In Fig. 2, a similar embodiment is shown except that carbonaceous formation 10 has been fractured by fractures 32. The operation of the well is basically the same as that shown in Fig. 1 except that carbonaceous formation 10 has previously been fractured or is fractured by a fluid which may comprise the aqueous oxidizing solution during at least part of the fracturing operation. For instance, it may be desirable to use a conventional fracturing application, if carbonaceous formation 10 is sufficiently impermeable, as an initial stimulation method followed by the aqueous oxidizing solution as a post-fracturing flush. The post-fracturing flush enhances the formation of free surfaces and cleats, and the release of adsorbed methane, throughout the areas contacting the fracture. In such instances, the well is desirably shut-in as discussed previously and the oxidants are selected from the same oxidant materials discussed previously. The fractures are formed in carbonaceous formation 10 prior to injection of the oxidizing solution. The oxidizing solution could comprise the fracturing fluid if desired. The aqueous oxidizing solution could also be injected above or below the fracture gradient (pressure) if desired.

In Fig. 3, an injection well 34 and a production well 36 penetrate carbonaceous formation 10 from surface 12. Injection well 34 is spaced apart from production well 36 at a spacing based upon the characteristics of the particular carbonaceous formation and the like. According to the present invention, the aqueous oxidizing solution described above is injected into carbonaceous formation 10 through injection well 34 as shown by arrow 26 and arrows 28 to treat zones 30 which may extend from injection well 34 in a generally circumferential direction, but generally extend preferentially toward a nearby production well or production wells. Production well 36 is positioned to withdraw water and methane from carbonaceous formation 10. The production of water and methane through production well 36 causes the aqueous oxidizing solution to migrate toward production well 36. Desirably, injection of the aqueous oxidizing solution is continued until an increased water volume is detected in production well 36 or until a desired increase in permeability or surface area or an increase in the volume of fluids produced is achieved. The increase in permeability, surface area or the volume of fluids produced from production well 36 is indicative of increased permeability, surface area or both in carbonaceous formation 10 and is attended by the release of additional quantities of fluids from carbonaceous formation 10 for production as shown by arrows 38 through production well 36 and an arrow 40. Arrows 38 are shown directed toward production well 36 from both directions in contemplation that water will continue to be recovered at a lower rate from untreated portions of carbonaceous formation 10.

The embodiment shown in Fig. 4 is similar to that shown in Fig. 3 except that carbonaceous formation 10 has been fractured by fractures 32. Fractures 32 in the embodiment shown in Fig. 2 can be of substantially any extent. By contrast, in the embodiment shown in Fig. 4, fractures 32 desirably extend no more than half way to production well 36. Clearly, if fractures 32 extend completely into production well 36, it will be difficult to use any kind of fluid or gas drive between injection well 34 and production well 36. Desirably, the fractures extend no more than half the distance between injection well 34 and production well 36. The use of the aqueous oxidizing solution with fractures 32 is as discussed previously.

In Fig. 5, a 5-spot well arrangement is shown. Multiple well arrangements, such as 5-spot well arrangements, are useful in the practice of the present invention and may be used in a recurring pattern over a wide area. Such arrangements are well known to those skilled in the art and will be discussed only briefly. In the arrangement shown in Fig. 5, the aqueous oxidizing solution is injected through injection well 34 to treat zones 30 to enhance the recovery of water and methane from the production wells 36. When the desired cleat formation or permeability increase has been achieved as evidenced by the production of fluids at an increased rate from production well 36, the injection of the aqueous oxidizing solution is stopped and injection well 34 can be converted to a production well. The area would then be produced through the original production wells and the converted injection well. The areas of zones 30 which have been treated will yield additional methane production rates and additional ultimate methane recovery.

The method of the present invention is also useful as a pre-treatment for gas injection treatments to enhance the recovery of methane from carbonaceous formation 10. The use of carbon dioxide, either alone or with other gases, to increase the production of methane from coal formations is well known. Similarly, the use of inert gases, such as nitrogen, argon and the like, to remove additional quantities of methane from the coal formations by increasing the pressure in the coal formation and thereby removing additional methane as the methane partial pressure in the atmosphere of the coal seam is decreased is well known to those skilled in the art. The use of such processes requires that the formation be permeable to gas flow into or through the formation so that the methane can be recovered, and also requires that the volumes of methane contained in the organic materials have available free surfaces through which to desorb. The method of the present invention enhances the formation of free surfaces and cleats in the organic materials, and enhances the permeability of the carbonaceous formation where the organic materials are more abundant and form continuous networks amenable to treatment, and may be used prior to the use of gas sweep or gas desorption treatments to enhance the recovery of methane.

While Applicants do not wish to be bound by any particular theory, the method of the present invention may function by creating free surfaces or a cleat system in the zones of carbonaceous formations contacted by the oxidizing solution. Generally the method of the present invention is effective to increase the surface area available for the desorption of methane from the macerals, kerogens and other inorganic materials present in the formation which contain quantities of methane. It appears that methane may be adsorbed to inorganic materials, particularly clays, as well as organic materials in such carbonaceous formations, and that the rate of methane production from both organic and inorganic materials is enhanced by the method of the present invention.

Having thus described the present invention by reference to certain of its preferred embodiments, it is noted that the embodiments discussed are illustrative rather than limiting in nature and that many variations and modifications are possible within the scope of the present invention. Many such variations and modifications may be considered obvious and desirable by those skilled in the art based upon a review of the foregoing description of preferred embodiments.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of increasing the rate of production of methane from a subterranean carbonaceous formation penetrated by at least one well, the method comprising:
   a) injecting an aqueous oxidizing solution containing at least one oxidant selected from the group consisting of peroxide, ozone, oxygen, chlorine dioxide, hypochlorite, water-soluble metallic salts of hypochlorous acid, perchlorate, chlorate, persulfate, percarbonate, permanganate, nitrate and combinations thereof into the formation;
   b) maintaining the aqueous oxidizing solution in the formation for a selected time; and
   c) producing methane from the formation at an increased rate.

2. A method of facilitating the release of methane from the surfaces of clay minerals in subterranean carbonaceous formations containing the clay minerals and penetrated by at least one well, said method comprising:
   a) injecting an aqueous oxidizing solution containing at least one oxidant selected from the group consisting of peroxide, ozone, oxygen, chlorine dioxide, hypochlorite, water-soluble metallic salts of hypochlorous acid, perchlorate, chlorate, persulfate, percarbonate, permanganate, nitrate and combinations thereof into the formation;
   b) maintaining the aqueous oxidizing solution in the formation for a selected time; and
   c) recovering methane from the formation.

3. A method as claimed in Claim 1 or Claim 2 where the water soluble metal salts are salts of sodium or potassium.

4. A method as claimed in Claim 3 wherein the aqueous oxidizing solution comprises an aqueous solution of at least one salt selected from perchlorates,

persulfates, perborates, percarbonates and permanganates of sodium and potassium.

5. A method as claimed in any one of claims 1 through 4, wherein the aqueous oxidizing solution is injected into the formation through a well; the well is shut-in for a selected time; and thereafter, methane is produced from the well at an increased rate.

6. A method as claimed in any one of claims 1 through 5, wherein the formation has been fractured with fractures extending from the well prior to injection of the aqueous oxidizing solution.

7. A method as claimed in any one of claims 1 through 6, wherein the aqueous oxidizing solution comprises a fracturing fluid injected at fracturing conditions to fracture the formation.

8. A method as claimed in any one of claims 1 through 7, wherein said aqueous oxidizing solution is maintained in the formation for at least 24 hours.

9. A method as claimed in any one of claims 1 through 8, wherein the oxidant is present in an amount up to the solubility limit of the oxidant in water.

10. A method as claimed in any one of claims 1 through 3 and 9, for the production of methane from a subterranean carbonaceous formation penetrated by at least one injection well and at least one production well, the method comprising:
  a) injecting the aqueous oxidizing solution into the formation through the injection well; and
  b) producing methane from the formation through the production well at an increased rate.

Fig.1.

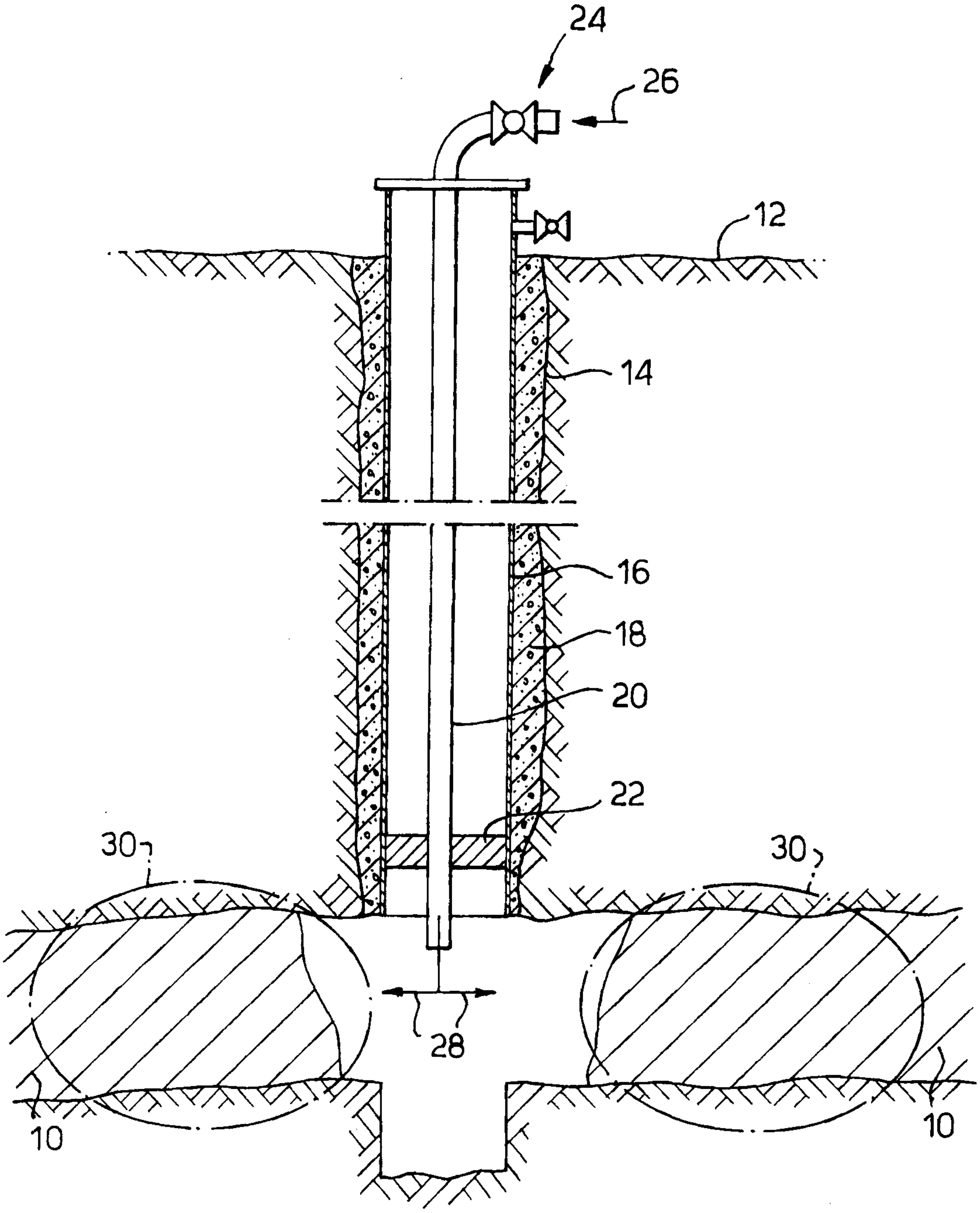
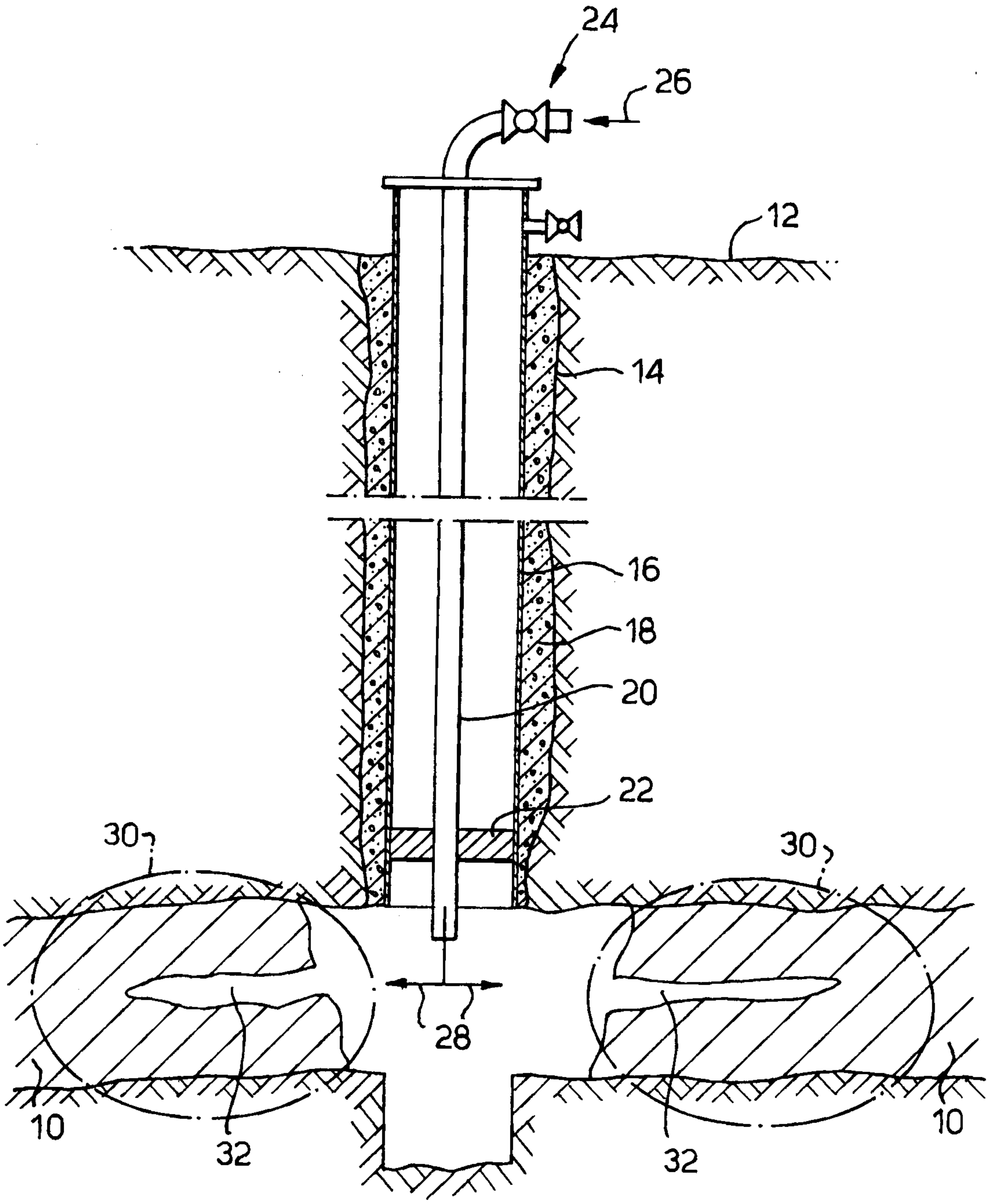


Fig.2.



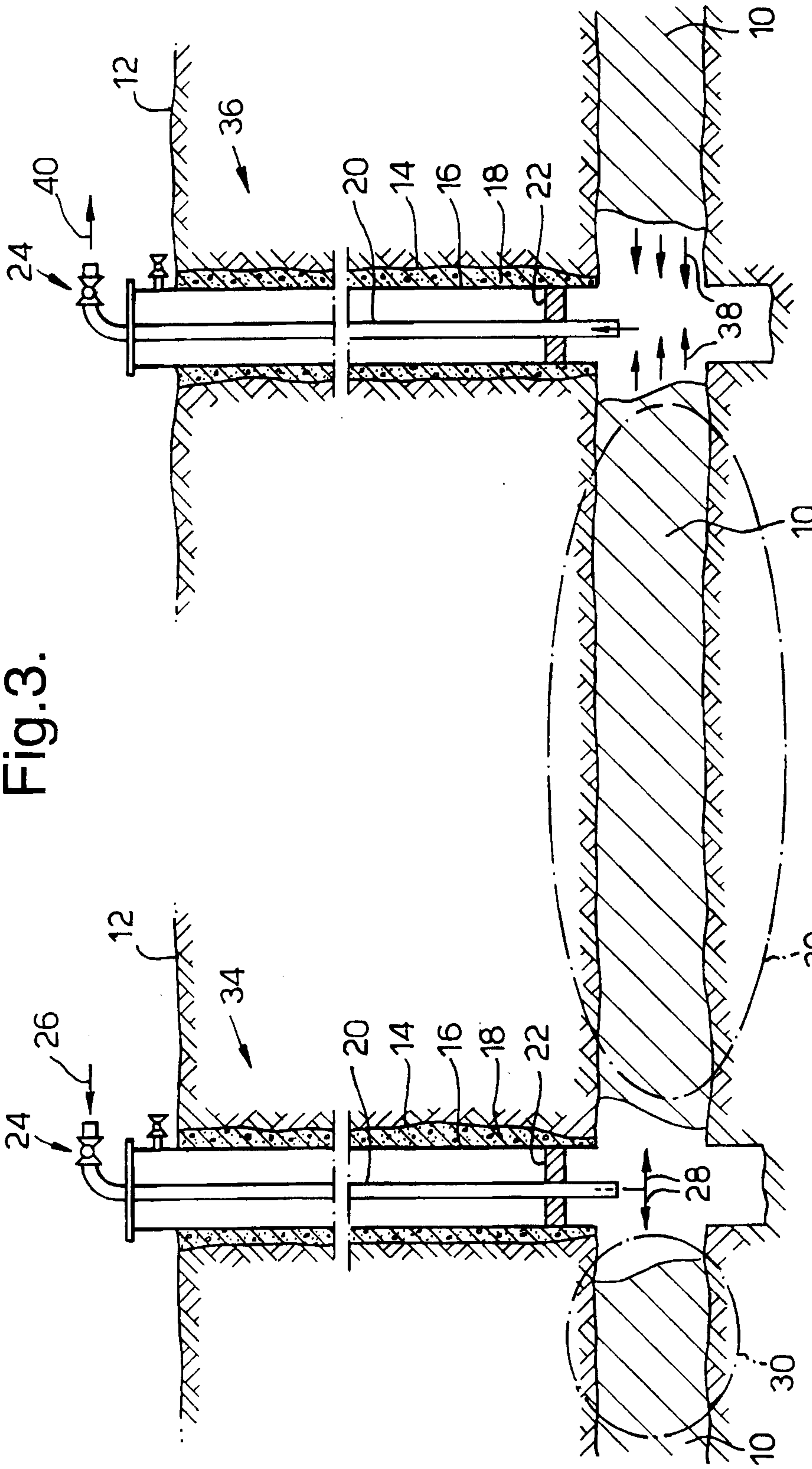

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Fig.3.

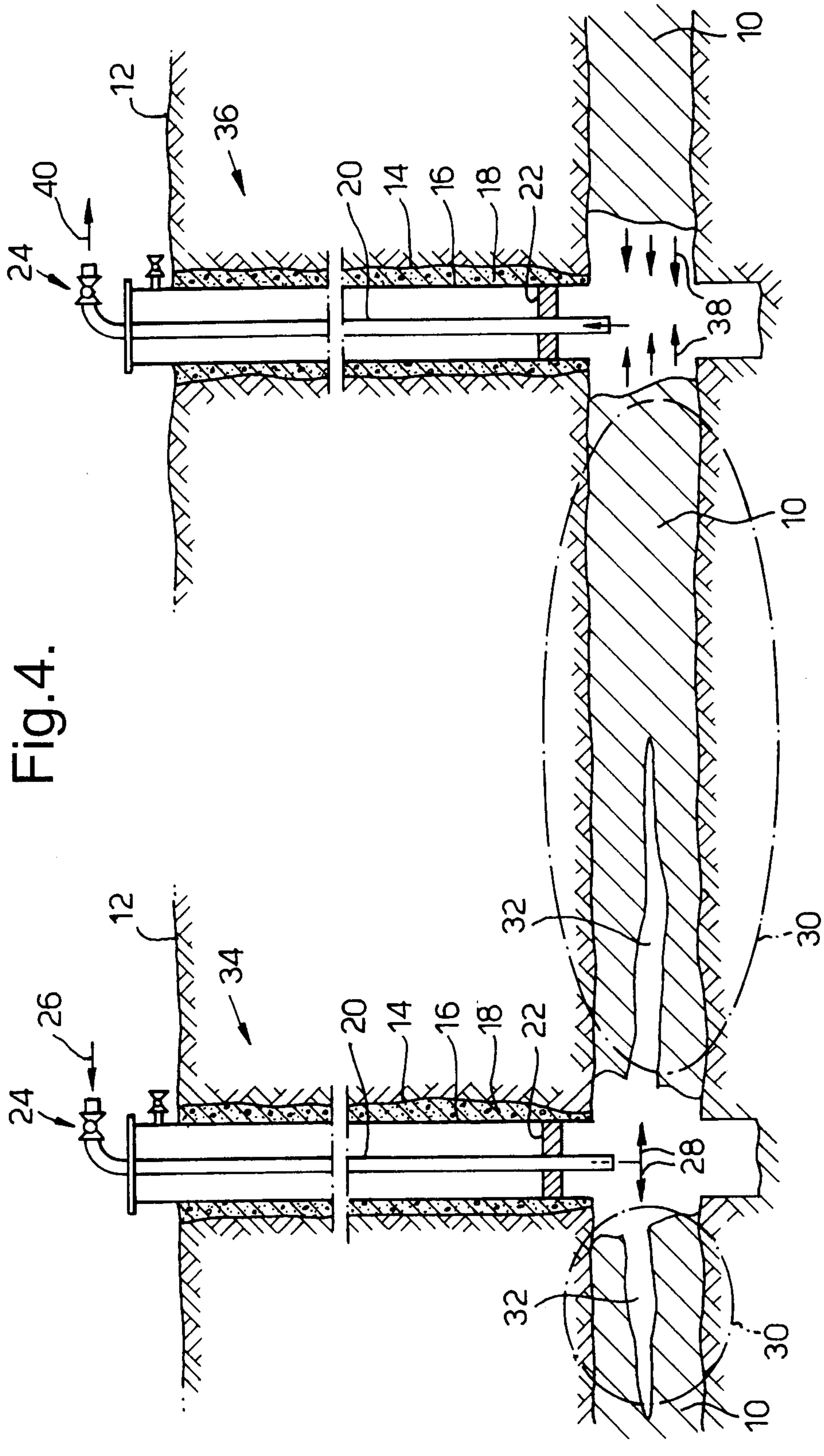
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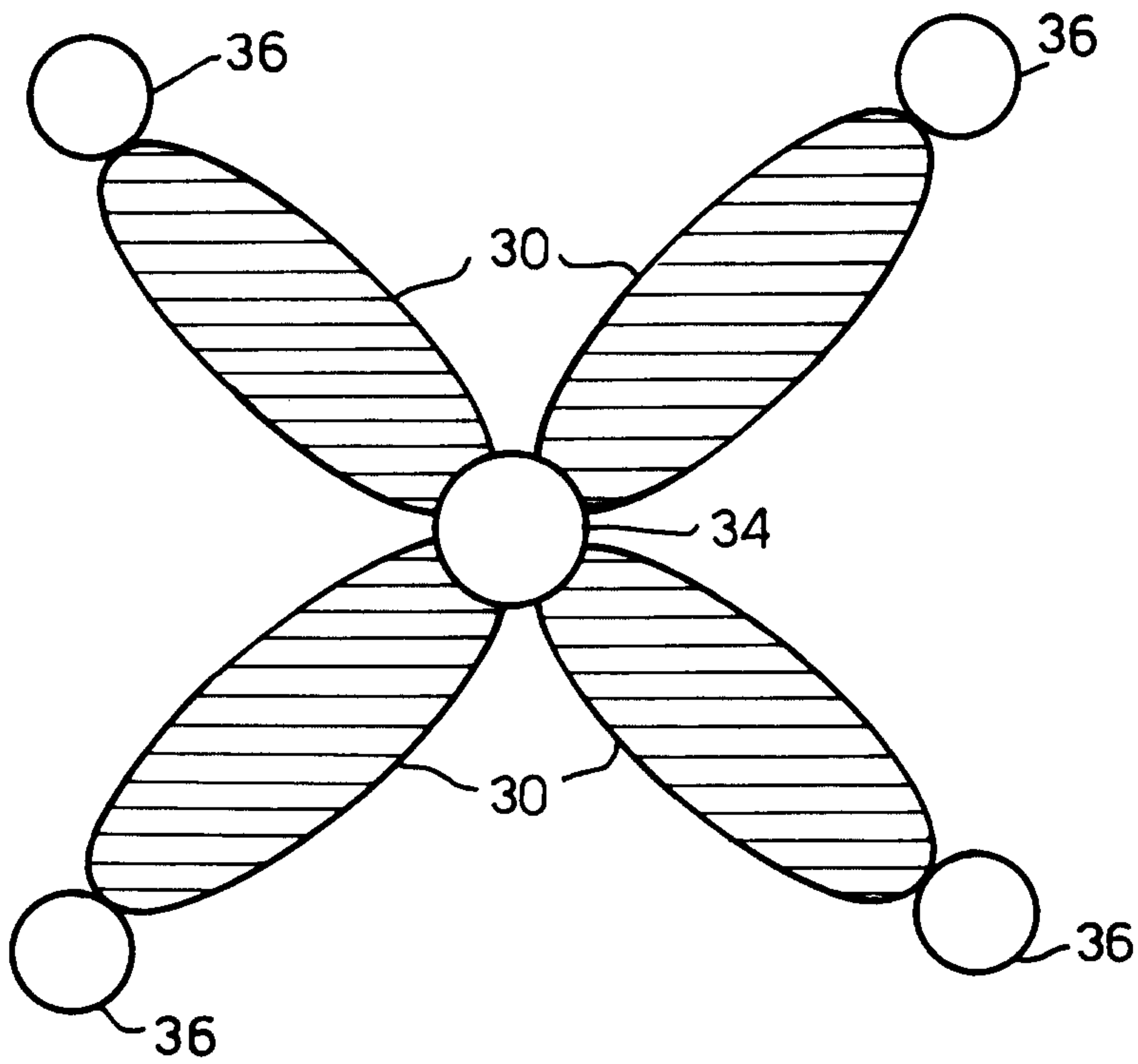
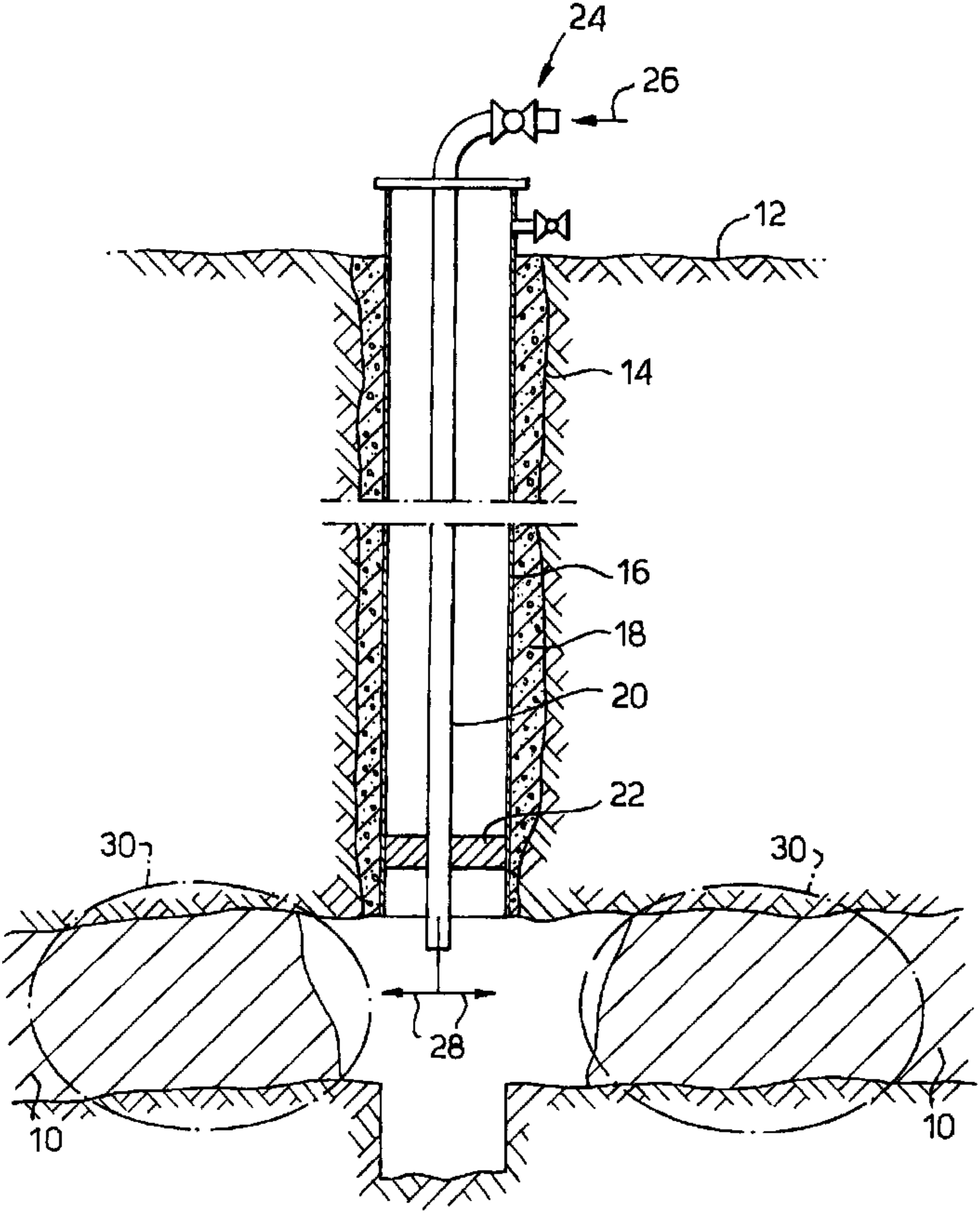
Fig.4.

Fig.5.

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