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(54) METHOD AND APPARATUS FOR OBTAINING DISSOLVED SUSPENDED OR CHEMICALLY BOUND SUBSTANCES FOR A LIQUID

(71) We, URANERZBERGBAU GMBH, a German Body Corporate of, 5300 Bonn, Kolnstrasse 367, Germany, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of and an apparatus for obtaining dissolved, suspended or chemically bound substances from a liquid. The invention is particularly, though not exclusively, useful for obtaining minerals, for example uranium or other heavy-metal compounds, from a liquid. It is known to pass liquid carrying desired substances in a substantially vertically ascending stream through a bed of adsorbent particles capable of adsorbing these substances.

Such a process, and apparatus for carrying it out, is suitable for example for obtaining uranium from the sea or from effluents. However, the concentration of uranium, and this applies also to other minerals, in sea water is so low that extraction on an industrial scale has not been seriously contemplated hitherto.

The known processes and apparatus, which employ beds of adsorbent granules or other particulate matter, heaped upon each other with an aqueous solution flowing between them so that ions contained in the solution are adsorbed on the surfaces of the adsorbent particles, which are wetted by the solution by reason of the active molecular forces display disadvantages. Thus, such adsorbent beds have an inherently large resistance to flow, which depends on the density and thickness of the bed. To this is added the fact that the adsorbent bed acts as a filter, which at least partly traps foreign solid matter, such as is always present in sea water, with the result that the resistance to flow increases over a period and the active surface area of the adsorbent particles is reduced. Of course, not all the surface area is available to be wetted in any case, because regions of the individual particles which lie against each other are not effective. A further disadvantage is the impossibility of carrying out a continuous process, which is a precondition for an economically viable operation.

It has, moreover, already been proposed to pass a liquid which contains a low concentration of uranium in solution, up through a column sub-divided into several chambers, each chamber containing a specific amount of a particulate adsorbent. The upward-flowing solution is intended to act in such a manner that a fluidised bed of particles is formed, that is to say, the particles are in turbulent motion in the stream within each chamber, the intention being to achieve as intensive a contact as possible between the solution and the surface of the particles, in the course of which the uranium is adsorbed from the solution. The flow velocity is to be so adjusted that as far as possible the adsorbent particles are nor carried upwards into the next chamber, nor do they sink down into the chamber located below. Although the application of this process makes the obtaining of uranium compounds technically achievable, it still has the disadvantage of inadequate profitability.

This can be attributed amongst other things to the fact that certain adsorbent materials erode severely, due to collision with each other, and on becoming smaller are carried out of the chambers and lost. The losses thus caused are so great that the process becomes uneconomical. In addition, with some adsorbent materials, the adsorbed substance deposits itself in a multi-molecular layer so that parts of the substance deposited may be subsequently rubbed off upon collision. This reduces the efficiency of the process to such an extent that the economics are questionable, while any possible continuous operation will require complicated technical installations and the specific energy consumption of the process is relatively high.

The aim of this invention is to provide an improved process and apparatus for obtaining dissolved, suspended or chemically bound substances from a liquid.

According to one aspect of the present invention there is provided a method of obtaining dissolved, suspended or chemically bound substances from a liquid, which comprises passing the liquid upwardly through a bed of adsorbent particles capable of adsorbing the substances, the bed being retained in a channel, wherein the specific gravity of the adsorbent particles is greater than that of the liquid, the flow velocity of the liquid on entry into bed is not less than the sedimentation velocity of those particles which have the highest sedimentation velocity and, on issuing from the bed, has a smaller effect on movement of the particles than that of the sedimentation velocity of those particles having the smallest sedimentation velocity, so as to provide a non-turbulent suspension of the particles, putting particles into the bed at a first point of the channel and withdrawing them at a second point thereof laterally separated from the first point, thereby causing a slow movement of the suspended particles across the channel in a direction transverse to that of the passage of the liquid through the bed, and, before the liquid is passed into the bed, flowing it through a device which provides a resistance to the flow which is at least a third of the resistance to the flow provided by the bed and varies over the cross-sectional area of the device so that the velocity of the liquid passing from the device to the bed is stabilised to become substantially uniform over its cross-section.

In another aspect the invention provides apparatus for use in obtaining dissolved, suspended or chemically bound substances from a liquid including a generally vertically arranged channel provided for holding non-turbulently a bed of adsorbent particles capable of adsorbing the substances, and having one or more input means for feeding fresh particles to the bed and one or more withdrawal means, laterally separated from the input means, for withdrawing particles from the bed and a device at the bottom of the channel to stabilise flow of liquid through the bed so that its velocity is substantially uniform across the bottom of the channel and to provide a resistance to the flow.

In effect, the invention provides for the adsorbent particles to move only slightly relative to each other within the liquid. As a result, contacts between the individual particles and/or between the latter and the walls of the apparatus will be reduced to a minimum. Practically all known granular adsorbent substances can be used, and their full surface areas can be employed. Also, a continuous operation is envisaged, according to a preferred feature, in that during their presence in the liquid, the adsorbent particles will move continuously from the input point to the withdrawal point.

According to a preferred feature, after passing through and being stabilised by the flow-resisting device, the liquid stream is slowed down uniformly due to a cross sectional enlargement of the channel in the manner of a diffuser.

A situation is achieved wherein the adsorbent particles remain quasi-stationary within the liquid, so that the particles collide with each other, and with the walls of the channel, to a lesser extent than previously or not at all. Thus, the occurrence of abrasion capable of reducing the particle size of the adsorbent material is of reduced probability, and that which does occur will be at low velocity, while substances already adsorbed are unlikely to be rubbed off.

If the deposition of the substance to be obtained on the individual particles remains so low that no appreciable increase in weight results, the particles will stay in suspension within the bed at a constant height. Since in fact the specific relative sedimentation velocity of each individual particle is just compensated at a particular level of the adsorbent bed by the upward flow of the liquid, the particles arrange themselves in layers depending on the factors influencing sedimentation velocity such as weight and shape of the particles, flow rate and the like. Within the layers the particle positions will not change substantially, as long as these major factors do not change. It is expedient to arrange the minimum and maximum flow velocities of the liquid within the channel, to define a range which includes the velocities corresponding to the extreme values of the expected relative sedimentation velocity of the adsorbent particles. It is then easier to withdraw particles of the bed at one side of a liquid stream, for instance continuously, and to feed in other particles for instance on the opposite side, again advantageously continuously. Thus, the bed formed by the particles in the stream at any one time constantly moves slowly across the channel from input point to withdrawal point. This means that the bed formed by the particles flows horizontally owing to a quantity gradient resulting from the removal of particles, in consequence of which a continuous operation becomes possible with one or more input points and one or more withdrawal points for the adsorbent particles. At the withdrawal point, the particles may be withdrawn over the entire height of the bed. It is possible also to withdraw the particles only in a lower region of the bed than the region of input. This would be useful when an adsorbent material is used which, in the course of deposition of the substance to be obtained, sinks in counter-current to the liquid stream into lower zones of the adsorbent bed, so that the lower layers of the bed contain the heavier particles. They can then be withdrawn through an appropriate withdrawal orifice or other device at a lower part of the channel.

The following description is given by way of example only with reference to the accompanying drawings in which:—

Fig. 1 shows a longitudinal section through a part of an apparatus according to the invention for obtaining substances from liquids;

Figure 2 is the perspective view of a ship equipped with an apparatus for obtaining substances from the sea;

Figure 3 is a side elevation of the ship and apparatus of Figure 2, partly in section; and

Figure 4 is a longitudinal section, corresponding to that of Figure 1, but of another embodiment.

The apparatus shown in Figure 1 includes a housing 11 bounding an upwardly extending channel 10 provided at the bottom with a screen, grate, sieve, perforated plate or the like 13. The channel 10 increases in cross sectional area in the upward direction. A loose bed 14 of adsorbent particles is provided in the channel, the particles, during operation being held in suspension by liquid flow indicated by the arrows 15. The flow velocity of the liquid decreases within the channel 10. The adsorbent particles, the specific gravity of which is greater than that of the liquid, have, to a first approximation, a sedimentation velocity which depends on the specific gravity of the particles and of the liquid, the size and external shape of the individual particles, the distances between individual particles and the viscosity of the liquid. When the sedimentation velocity specific to each individual particle is just compensated by the upward flow of the liquid, that particle remains in suspension. Accordingly, within the upward flowing liquid stream the adsorbent particles arrange themselves approximately in layers at heights on their sedimentation velocity, and do not change their position substantially in the vertical direction, as long as the factors determining sedimentation velocity do not undergo any change. Where particles are grouped close to each other they influence each other's movement so that the sedimentation velocity of the group is less than that of the individual particles. In the embodiment illustrated in Figure 1, the flow velocities of the liquid at the bottom and at the top of the channel will define a range which includes velocities corresponding to the extremes of the expected sedimentation velocities of the adsorbent particles, so that the top and the bottom boundaries of the bed 14 are located within the channel 10.

The embodiment of Figure 4 is the same as that of Figure 1 except that the inside walls of the housing 111 which define the channel 110 are parallel to each other. The *free* cross-section of the channel, i.e. that through which the liquid can pass, is still greater at the top of the channel. That is, the bed itself presents a smaller cross-section than the channel above it. A further possibility is to have a channel with a lower region bounded by parallel walls and an upper region which increases in cross sectional area in the upward direction.

The grate, sieve or the like 13 which forms the bottom boundary of the channel 10 has a specific resistance to flow, which is at least a third and in some cases at least a half as great as the resistance to flow of the bed 14.

The magnitude of the resistance to flow of the grate or the like determines the stability of the flow profile within the adsorbent bed. However, for reasons of conservation of energy it should be kept at a low level consistent with good flow conditions in the adsorbent bed.

Since the resistance to flow of the grate varies over the surface area of the grate, a practically complete homogeneity of the flow velocity in close proximity above the grate can be achieved. The resistance to flow of the grate or the like 13 can be reckoned approximately in the following manner:

$$W_{Grate}=\left(\frac{F_g}{\mu . F_{free}}-1\right)^2 . d . \frac{U^2}{2}$$

wherein

W_{Grate}=the total resistance to flow of the grate, sieve or the like, 13,

F_g=the total grate surface area,

F_{free}=the sum of the areas of the apertures in the grate,

μ=a factor between 0.5 and 1, which takes account of the influence of the aperture shape,

d=the specific gravity of the liquid,

U=the velocity of the flow, relative to the grate.

In the embodiment illustrated in Fig. 1 of the drawing, the upper end of the housing 11 delimiting the diffuser channel 10 is also provided with a sieve or the like 12 which, however, is merely intended to prevent the transport of adsorbent particles upwards out of the diffuser in the case of any unforeseeable and/or uncontrollable factors occurring. It is of course also possible to mount this sieve or the like 12 at some other location, that is to say, at a greater distance from the diffuser in a conduit for the outflowing liquid. Since, as already explained, the occurrence of appreciable abrasion and resulting erosion need not be feared, the sieve 12 may have a mesh or aperture size which does not substantially increase the resistance to flow.

The channel 10 is provided with stabilisers 16, which project from above into the bed 14. The stabilisers may be constructed as for instance plates or pipes. They are intended to effect a further homogenisation of the flow velocity in the diffuser channel 10 within the region of the adsorbent bed 14, and usually arranged substantially parallel to the directions of flow of a liquid when passed through the channel. Should a local increase of flow velocity occur, caused for example by accidental differences in density or differences in the overall height of the adsorbent bed, it would not be possible to exclude the possibility, in the absence of stabilisers, that the flow velocity in the other regions would fall, with the result that at these locations the adsorbent particles would sink and particles from other regions would be drawn in. The packing of the bed in these regions would then become denser, leading to increasing resistance to flow and a further fall in flow velocity. At other regions, an approximately tubular channel of increased flow velocity might form. The stabilizers subdivide the bed 14 in its upper region into sections and make it more difficult for particles to move horizontally in that region. If an increase in flow velocity occurs at certain locations, the adsorbent bed rises in the sections thus affected. This results in an increase of the resistance to flow, owing to which the flow at these locations is slowed down and is regulated relative to the overall cross-section of the diffuser.

In the embodiment of Fig. 1, it is to be assumed that the adsorbent particles are fed laterally to the channel via input means (not shown). When adequately charged with the substance to be obtained they are withdrawn laterally, in particular either over the entire height of the bed or in the lower region of the bed, through withdrawal means (not shown). In the latter case, it is expedient to use an adsorbent which, in the course of adsorption of the substance to be obtained, experiences such a weight increase that it sinks downwards within the bed. The saturated particles would be withdrawn laterally approximately at the level of the lower boundary of the bed 14.

Fig. 2 shows a possible embodiment of a complete apparatus for obtaining substances from the sea. The semi-submergable ship body 20, which may be towed by a mother ship or anchored in a suitable current, for example the Florida current, carries on both sides outriggers, in which the adsorbent beds constructed as shown in Fig. 1 are arranged. As can be seen in Fig. 3, the beds may each be subdivided into an inlet bay 21 and a return bay 22. Fresh, unsaturated adsorbent material is fed continuously or discontinuously from the ship's body 20 into the inlet bay 21, whilst saturated adsorbent material is withdrawn at the same rate and/or in the same quantity from the return bay 22 into the ship's body 20. At the free ends 23 and 24 (Fig. 2) the inlet and return bays of an adsorption bed unit 23 are interconnected, so that the adsorbent material can pass from the inlet bay into the return bay. This means that the bed is preferably continuously in movement from the ship's body 20 to the end of the outrigger and back again in a substantially horizontal plane. Since the bays 21 and 22 on one side of the ship together form an approximately U-shaped channel, the input and withdrawal points for this channel at the ship's body are approximately side-by-side.

On the ship's body 20 guide surfaces or vanes 26, are arranged in such a manner, that one is associated with each inlet bay or each inlet orifice. These guide surfaces 26 are adjustable, so that the currents in the individual inlet bays 21 of both outriggers or in the inlet orifices of these inlet bays can be regulated.

The saturated adsorbent material is eluted in the ship's body 20 or, optionally, in a mother ship or factory ship, to recover the adsorbed substances, and is then returned to the cycle. It is also feasible to carry out the elution process in the ship's body and to integrate the device used for this purpose in a cyclic stream for the adsorbent material, which stream also comprises the previously described devices and beds.

An example of an experimental arrangement will be described below:

An experimental diffuser channel was used, which measured 300x1,500 mm at its narrowest cross-section, whilst its walls diverged at an angle of 6° relative to the vertical axial direction.

A sieve, arranged in the narrowest cross-section of the diffuser, consisted of a perforated plate, the apertures of which had a diameter of 1.5 mm. The ratio of the total open area of the apertures to the total surface area of the sieve was 0.12, and apertures were provided in greater numbers per unit area of the sieve at the edges than in the centre.

Placed within the diffuser channel was a heap of adsorbent particles with a height 150 mm. The material of the particles had a specific gravity of 2.25 g/cm³. The individual particles had diameters of 1 to 3 mm, the particle size distribution being approximately uniform.

Sea water then passed from below perpendicularly against the sieve.

At a water throughput rate corresponding to a flow velocity of approximately 2 cm/sec, relative to the sieve, the bed began to be fluidised. At a water throughput rate corresponding to a flow velocity of approximately 7 cm/sec, relative to the sieve, the particle bed was so dispersed that its volume increased by 40% compared with its undisturbed volume. A strong segregation of the particles according to particle size took place, in the course of which the larger particles were supported near the bottom of the diffuser channel and the smaller particles at the top. The smaller particles displayed only 1 to 3 cm variation in level within the channel while the flow was maintained.

The surface of the suspended particle bed showed slight local oscillation, but this was generally uniform over the whole width of the bed.

During the experiments, dyestuff-marked particles (approximately 10 Kg.) were fed in at one side of the suspended bed over a period of approximately 10 seconds. It was observed that these marked particles pushed the original particles in front of them and the particle distribution as well as the height of the bed became uniform over the entire width of the bed within a few seconds.

When, on the other side of the bed, approximately 10 Kg. of particles were withdrawn by suction, the uniformity of the particle distribution was again re-established very rapidly.

A horizontal migration of the particles was seen to occur substantially only during addition and/or take-off of particles, it being unnecessary to effect the input and the withdrawal simultaneously. The mixing of particles in the bed, with new particles fed in from one side proceeds very slowly.

Analyses of the particles and of the sea water passed through proved that good conditions for material transfer in a quasi-stationary suspended adsorbent particle bed prevail, since up to 90% of the heavy metals present in the water were adsorbed by the particles during passage through the latter.

WHAT WE CLAIM IS:—

1. A method of obtaining dissolved, suspended or chemically bound substances from a liquid, which comprises passing the liquid upwardly through a bed of adsorbent particles capable of adsorbing the substances, the bed being retained in a channel, wherein the specific gravity of the adsorbent particles is greater than that of the liquid, the flow velocity of the liquid on entry into bed is not less than the sedimentation velocity of those particles which have the highest sedimentation velocity and, on issuing from the bed, has a smaller effect on movement of the particles than that of the sedimentation velocity of those particles having the smallest sedimentation velocity, so as to provide a non-turbulent suspension of the particles, putting particles into the bed at a first point of the channel and withdrawing them at a second point thereof laterally separated from the first point, thereby causing a slow movement of the suspended particles across the channel in a direction transverse to that of the passage of the liquid through the bed and, before the liquid is passed into the bed, flowing it through a device which provides a resistance to the flow which is at least a third of the resistance to the flow provided by the bed and varies over the cross-sectional area of the device so that the velocity of the liquid passing from the device to the bed is stabilised to become substantially uniform over its cross-section.

2. A method according to claim 1, wherein input and withdrawal of the adsorbent particles to and from the channel are carried out continuously.

3. A method according to claim 1 or 2 wherein the liquid is water.

4. A method according to claim 3 wherein the water is seawater.

5. Apparatus for use in obtaining dissolved, suspended or chemically bound substances from a liquid including a generally vertically arranged channel provided for holding non-turbulently a bed of adsorbent particles capable of adsorbing the substances, and having one or more input means for feeding fresh particles to the bed and one or more withdrawal means, laterally separated from the input means, for withdrawing particles from the bed and a device at the bottom of the channel to stabilise flow of liquid through the bed so that its velocity is substantially uniform across the bottom of the channel and to provide a resistance to the flow.

6. Apparatus according to claim 5 wherein the channel increases in cross sectional area in the upward direction.

7. Apparatus according to claim 5 or 6 wherein the channel has at least two opposed vertical walls of the channel are vertical.

8. Apparatus according to claim 5 wherein the channel is bounded in its lower

region by walls of which at least two opposite walls are parallel to one another and the channel is in its upper region divergent in the manner of a diffuser.

9. Apparatus according to any one of claims 5 to 8 wherein the device is one of a screen, a sieve, a grating and a perforated plate.

10. Apparatus according to any one of claims 5 to 9 wherein the resistance to flow provided by the device increases from its periphery towards its centre.

11. Apparatus according to any one of claims 5 to 10 including stabilisers arranged in at least the upper part of the channel substantially parallel to the direction of flow of a liquid when passed through the channel.

12. Apparatus according to claim 11 wherein the stabilisers are supported from above and extend into the upper region of the channel.

13. Apparatus according to claim 11 or 12 wherein the stabilisers are constructed as plates or pipes.

14. Apparatus according to any one of claims 5 to 13 including means for continuously feeding adsorbent particulate material to, and removing it from, the channel.

15. Apparatus for use in obtaining dissolved suspended or chemically bound substances from a liquid, such apparatus being constructed and arranged substantially as hereinbefore described with reference to and as illustrated in Figure 1 of the accompanying drawings.

16. Apparatus for use in obtaining dissolved suspended or chemically bound substances from a liquid, such apparatus being constructed and arranged substantially as hereinbefore described with reference to and as illustrated in Figure 4 of the accompanying drawings.

17. Apparatus for use in obtaining dissolved suspended or chemically bound substances from a liquid, such apparatus being constructed and arranged substantially as described in the Example herein.

18. Apparatus according to any one of claims 5 to 17 including a bed of adsorbent particles in the channel.

19. A method of obtaining dissolved suspended or chemically bound substances from a liquid substantially as hereinbefore described with reference to Figure 1 of the accompanying drawings.

20. A method of obtaining dissolved suspended or chemically bound substances from a liquid substantially as hereinbefore described with reference to Figure 4 of the accompanying drawings.

21. A method of obtaining dissolved suspended or chemically bound substances from a liquid substantially as described in the Example herein.

22. Apparatus according to any one of claims 5 to 18 when used in performing the method of any one of claims 1, 2, 3, 4, 19, 20 and 21.

23. A ship having a plurality of outriggers in each of which apparatus according to any one of claims 5 to 18 is provided.

24. A ship constructed and arranged substantially as hereinbefore described with reference to and as illustrated in Figures 2 and 3 of the accompanying drawings.

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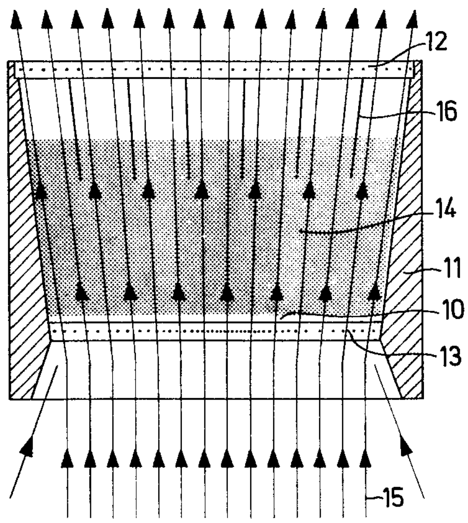
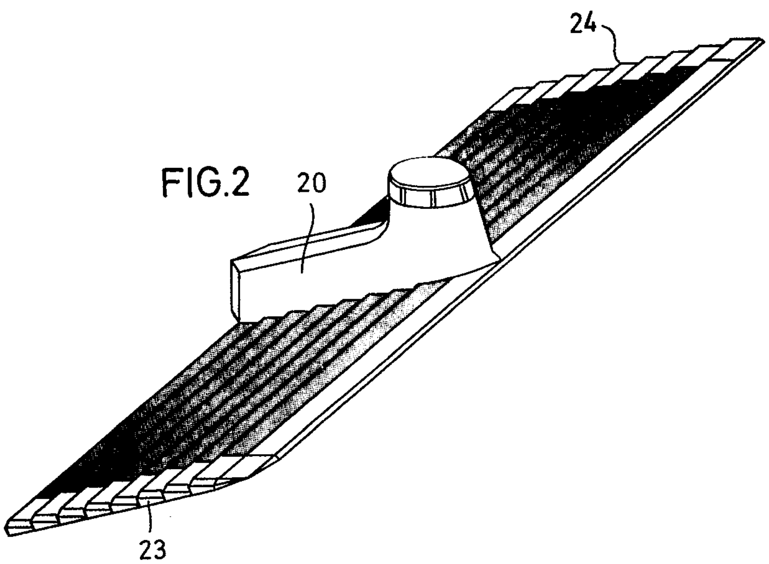


FIG. 1

FIG.2



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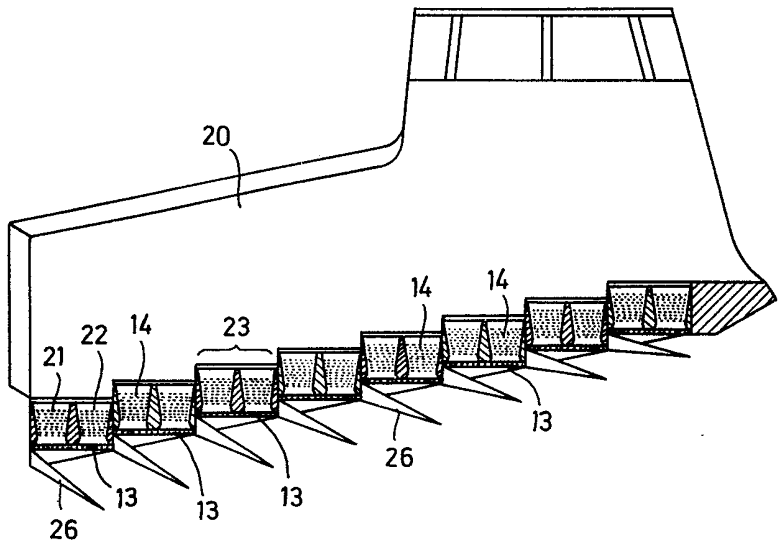
3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 2

FIG.3



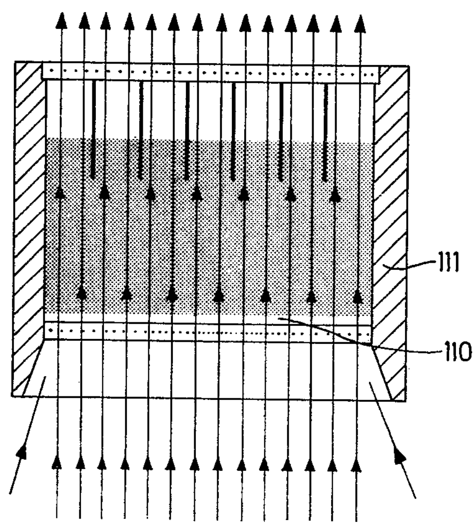


FIG.4