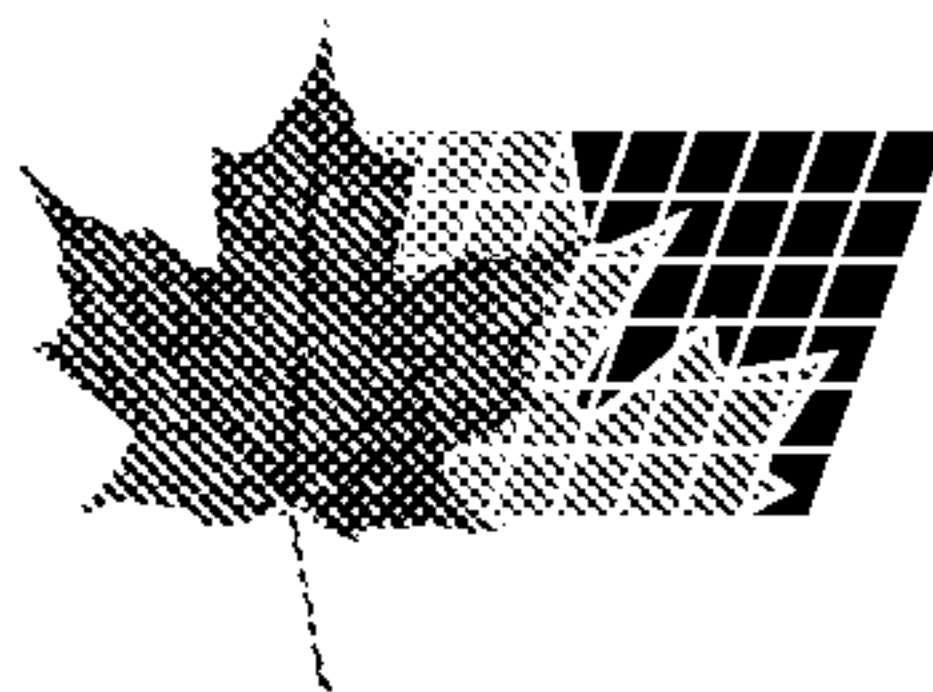




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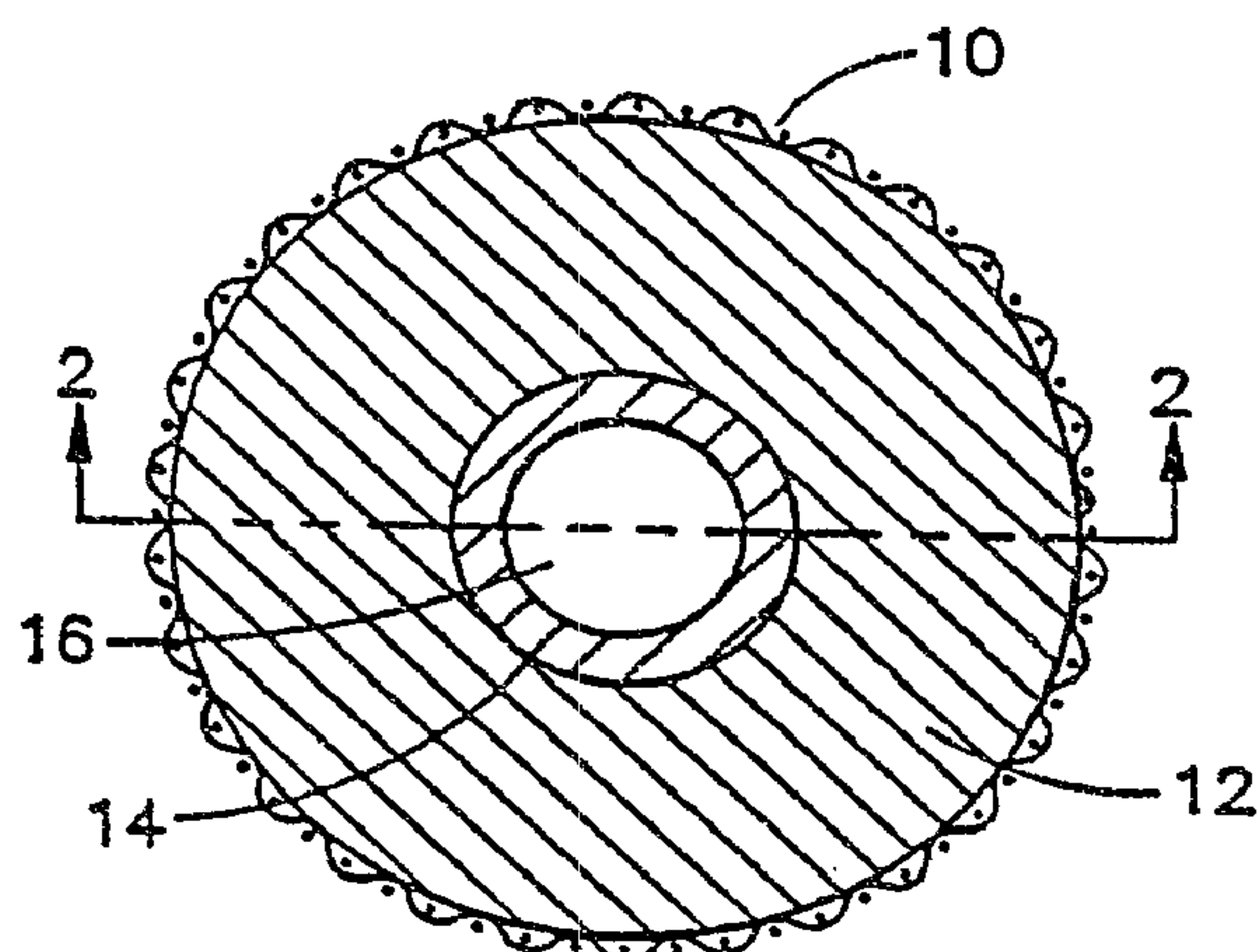
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(54) **METHODE ET DISPOSITIF POUR L'OBTENTION DE
REACTIONS RAPIDES DANS UN REACTEUR A REACTIFS
SOLIDE ET GAZEUX**

(54) **METHOD AND APPARATUS FOR ACHIEVING HIGH
REACTION RATES IN SOLID-GAS REACTOR SYSTEMS**



(57) Les taux de réaction de chimiosorption impliquant des agents de réaction solides et des ligands gazeux sont améliorés à l'aide d'un procédé qui maintient une densité optimisée de l'agent de réaction solide et/ou du produit de réaction en limitant son expansion volumétrique pendant la réaction. Un appareil de mise en oeuvre du procédé comprend une ou plusieurs chambres de réaction ayant des moyens de commande de l'expansion volumétrique se présentant sous la forme de parois poreuses (10) et de surfaces (12) de support de l'agent de réaction, les parois ou les surfaces ou encore les deux pouvant être mobiles et biaisées pour maintenir le contact avec l'agent de réaction solide et les produits de réaction et restreindre leur expansion volumétrique pendant la réaction de chimiosorption. Un fluide d'échange thermique approprié passe le long de l'intérieur (16) du tube de transfert de chaleur (14).

(57) Reaction rates in chemisorption reactions involving solid reactants and gaseous ligands are improved by a process for maintaining optimized density of the solid reactant and/or reaction product by limiting to volumetric expansion thereof during the reaction. An apparatus for carrying out the process comprises one or more reaction chambers having volumetric expansion control means in the form of porous walls (10) and reactant support surfaces (12), either or both of which may be movable and biased, for maintaining contact with solid reactant and reaction products and restricting the volumetric expansion thereof during the chemisorption reaction. A suitable heat exchange fluid passes along the interior (16) of heat transfer tube (14).

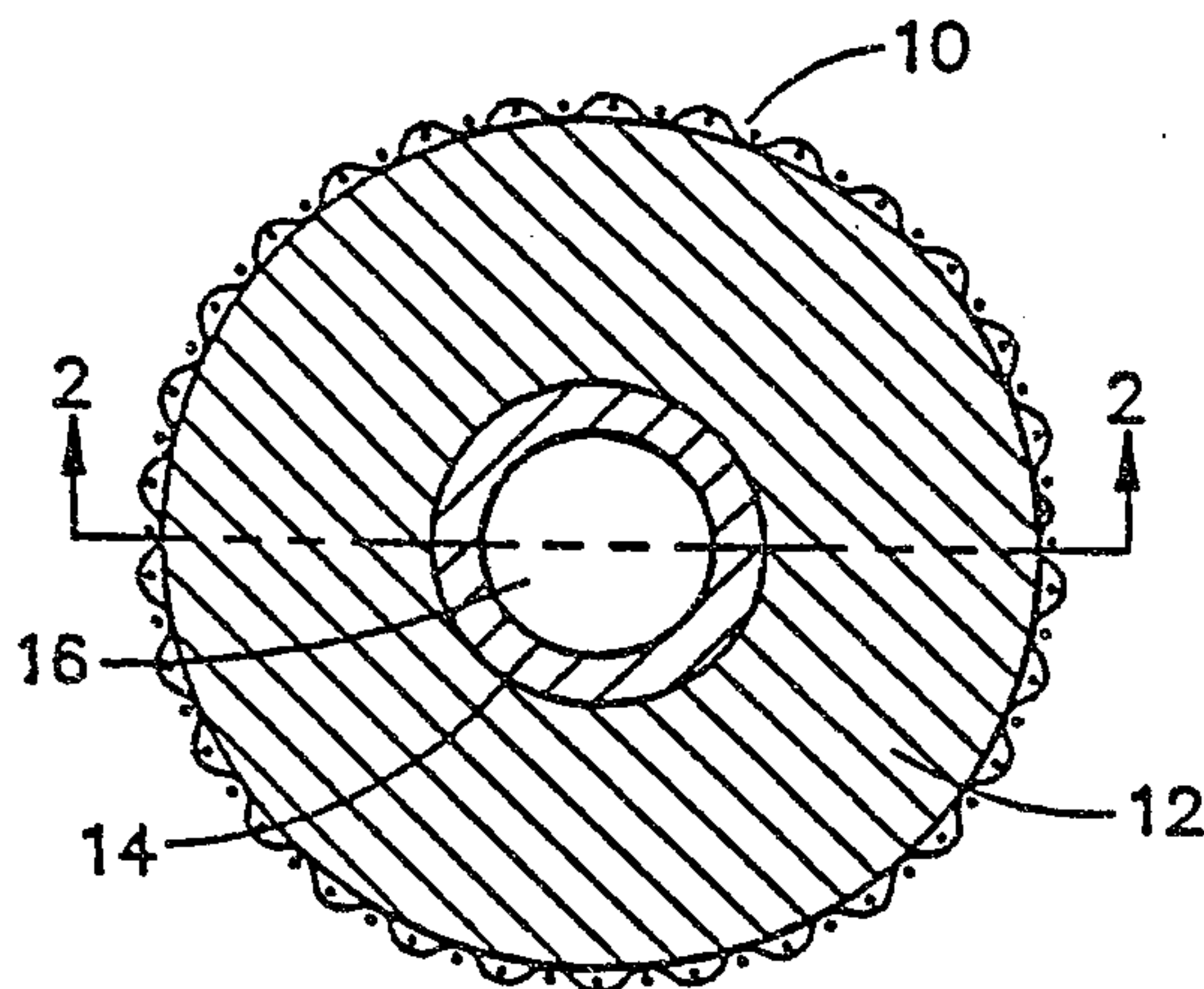


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(57) Abstract

Reaction rates in chemisorption reactions involving solid reactants and gaseous ligands are improved by a process for maintaining optimized density of the solid reactant and/or reaction product by limiting to volumetric expansion thereof during the reaction. An apparatus for carrying out the process comprises one or more reaction chambers having volumetric expansion control means in the form of porous walls (10) and reactant support surfaces (12), either or both of which may be movable and biased, for maintaining contact with solid reactant and reaction products and restricting the volumetric expansion thereof during the chemisorption reaction. A suitable heat exchange fluid passes along the interior (16) of heat transfer tube (14).

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**METHOD AND APPARATUS FOR ACHIEVING HIGH REACTION RATES IN
SOLID-GAS REACTOR SYSTEMS**

BACKGROUND OF THE INVENTION

The use of complex compounds, zeolites, activated
5 carbon, metal hydrides and metal oxide-hydroxide reaction
compositions as heat pump working materials is known in the
art. Complex compounds are materials formed by adsorption of
gas molecules on a solid adsorbent. Suitable complex compounds
comprise metal salts on which gaseous ligands such as water,
10 ammonia, methanol, methane, ethane and the like are alternately
adsorbed and desorbed. A number of such materials are
described in U.S. patent nos. 4,822,391, issued April 18, 1989
and 4,848,994, issued July 18, 1989. These complex compounds
are highly advantageous in heat pump technology, thermal
15 storage or in other heat-transfer systems, since they are
relatively inexpensive, yield higher refrigerant density as
compared to liquid-vapor media, and are useful in relatively
simple and inexpensive heat pump apparatus.

Other solid-gas reaction systems, such as metal
20 hydrides, inclusion compounds (zeolites and activated carbons),
and metal oxide-hydroxide and metal oxide-carbonate reactions
have application as heat pumps, refrigeration and power cycle
working media, desiccants, scrubbers, adsorbents for solvent
recovery, or thermal energy storage. The subject invention is
25 applicable to all such systems.

Solid-gas adsorption and desorption reactions are
generally accompanied by significant volume and density changes
of the solid material. Such solid-gas reactions are typically
conducted in fluidized beds, on flat plate heat exchange
30 surfaces on which the solid reactant, is located, or with heat
transfer and gas flow tubes embedded in a mass of

solid reactant. These systems allow free expansion of the solid reactant. However, if the solid is allowed to expand without restriction, a large void fraction results thereby substantially reducing composition density with concomitant reduction of thermal conductivity and reaction rates because of limited heat transfer in the solid mass and at the interface. It is an object of the present invention to reduce or obviate such problems.

SUMMARY OF THE INVENTION

10 The present invention comprises a method and apparatus for containing a solid reactant in a fixed volume reactor at optimum density not maintainable in conventional reactor systems while providing sufficient heat conduction whereby thermal paths are short and mass diffusion path length is independent of thermal path lengths. High density of the solid with concomitant increased thermal conductivity of the reactant and multiple thermal conduction paths provides a cost-effective means of decreasing reaction rate limitations imposed by poor heat transfer. These as well as other advantages will be evident from the following
20 detailed description.

 Thus, a first aspect of the present invention provides a process comprising a chemisorption reaction in which a gaseous reactant is alternately adsorbed and desorbed on a solid reaction product formed by adsorbing the gaseous reactant on a solid reactant, the reaction product having an increased or decreased volume as compared to the solid reactant,

wherein the reaction rate of the chemisorption reaction is increased by maintaining optimized density of the solid reaction product during the reaction by contacting the solid reactant and reaction product with volumetric expansion control means during at least a portion of the chemisorption reaction whereby expansion of at least one of the solid reactant and the solid reaction product is limited so as to improve the reaction rate of the process.

10 A second aspect of the present invention provides a reaction apparatus comprising:

 one or more reaction chambers for containing a solid reactant and a gaseous reactant exposed to the solid reactant and for reacting therewith to form a solid reaction product having an increased or decreased volume as compared to the volume of the solid reactant prior to the reaction; and

 movable volumetric expansion control means for contacting the solid reactant and the reaction product and optimizing the density thereof during the reaction by limiting the
20 volumetric expansion thereof.

 A third aspect of the present invention provides a method of increasing the reaction rate of a chemisorption reaction process, wherein a gaseous reactant is alternately adsorbed and desorbed on a complex compound formed by adsorbing the gaseous reactant on a solid reactant, the complex compound being capable of having a first density when allowed to expand without restriction during the adsorption; and the density of the complex compound is maintained at a second density greater than the first density during the reaction process.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a top view of a first embodiment of the invention incorporating a series of plates spaced along a heat transfer tube with a column of wire mesh volumetric restraining means secured around the periphery of the trays;

Fig. 2 is a sectional view taken along lines 2-2 of Fig. 1;

Fig. 3 illustrates another apparatus embodiment comprising a plurality of reaction chambers defined within an enclosed tubular wall with spaced plates secured therealong and incorporating a concentric perforated tube for directing gas to and from the reaction chambers;

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Fig. 4 is a partial sectional view taken along lines 4-4 of Fig. 3;

Fig. 5 illustrates an apparatus modification incorporating layers of spaced reactor beds in which the spaced reactor bed plates are secured within an elongated tube comprising the volumetric restriction means;

Fig. 6 is a sectional view taken along lines 6-6 of Fig. 5;

Fig. 7 illustrates another embodiment incorporating a porous sleeve along a heat transfer tube to provide a second path for gaseous reactant,

Fig. 8 is a sectional view taken along lines D-D of Fig. 7;

Fig. 9 is a side view showing another embodiment incorporating upper and lower layers of solid complex compound held against a central heat exchanger by volumetric expansion restriction means;

Fig. 10 is a sectional view showing yet another embodiment using multiple heat transfer plates separating layers of a solid-gas complex compounds all secured within volumetric expansion restriction means;

Fig. 11 is an end view illustrating yet another embodiment of the invention incorporating a column of solid reactant surrounding a heat transfer tube with a volume restraining wire mesh surrounding the column;

Fig. 12 is a sectional view taken along lines 12-12 of Fig. 9,

Figs. 13-17 are graphs showing comparisons of reaction rates of various complex compounds using the system of the invention vs. free, uncontrolled expansion.

DETAILED DESCRIPTION OF THE INVENTION

Solid-gas or solid-vapor reactants comprise complex compounds which normally expand in volume between about 1.5 and about 10 times as the gas moiety is adsorbed into the

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solid component. The improvement of the invention in maintaining optimum reaction density by restricting volumetric expansion is particularly advantageous for systems incorporating the substantially expanding solids. In another
5 embodiment of the invention in which solid compositions having relatively low expansion are used, the compositions are initially packed into the reaction chamber at density greater than the free, unpacked pour density, and maintained at the higher density throughout the reaction. In other substances,
10 such as metal hydrides, inclusion compounds, and metal oxides, volumetric expansion ranges from that of the aforesaid complex compounds to near zero.

Salts which adsorb gaseous ligands and which are useful for the aforesaid purpose include nitrites, nitrates,
15 oxalates, sulfates, sulfites and halides, particularly chlorides, bromides and iodides of alkali metals, alkaline earth metals, transition metals, zinc, copper, cadmium, tin and aluminum. Magnesium and manganese salts are also particularly useful as are double salts of the above metals gold, silver and
20 cobalt with oxides of calcium, sodium, strontium, magnesium and manganese oxide. These salts are disclosed generally in the aforesaid U.S. patents.

Complexes of these salts with ammonia, water, methanol and other lower alkanols, sulfur dioxide, polyamines,
25 particularly lower alkyl diamines, carbon dioxide, phosphine and methylamine are most useful, although any of the aforesaid compounds are intended to be included within the scope of the invention.

As the complex compounds are formed by adsorption of
30 the gaseous ligand on the solid material, substantial heat is created. This energy is to be recovered in the reactor by heat transfer plates, tubes or other heat exchange surfaces of the

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apparatus. Conversely, when the complex releases a portion or all of the gas moiety during a desorption phase, the solid complex decreases in volume, but to a lower extent, and at the same time absorbs heat, again with the energy being transferred through the heat exchange surfaces to which the compounds are exposed in the reactor. During such sorption reactions, it is important to maximize the reaction rates. Reaction rates are controlled by thermal conductance, mass transfer and intrinsic kinetics. Such rates are maximized by achieving high thermal conductivity of the solid for the energy transfer while also maintaining adequate porosity for diffusion or transfer of the gas. If the solid is allowed to expand without restraint, large void fractions in the solid structure result causing substantially reduced thermal conductivity thereby limiting the heat transfer and reaction rates. By maintaining density of the solid reactant different and typically greater than that of the reactant in its free sorbed state an optimal balance between thermal conductivity and porosity is achieved and reaction rates are maximized. Thus, the loading density of the unreacted solid sorbent is very important in obtaining preferred results.

According to the invention, these improvements and advantages are realized by maintaining the solid reactants at their optimum reaction densities during the reactions by restricting the volumetric expansion of the expandable solid complex compounds. More specifically, the volume of the reaction chambers in which the complex compounds are contained during reaction are limited by providing reactant containment means which creates closely spaced thermal conduction paths and also allows for passage of the reacting gases to and from the solid reaction adsorbent. The containment means comprises

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a variety of materials including wire mesh, perforated plates or tubing, or other materials including foams porous to gas. These materials are provided on at least one or more walls or barriers defining and surrounding the reaction chamber. The
5 remainder of the

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walled reaction chamber may be the heat exchange surface and/or the conduit for the heat exchange fluid. Using such reaction chambers allows for adequate exposure and transfer of the gas into and from the solid reaction mass from outside of the reaction chamber, while at the same time affording good heat transfer within the reactor to and from the solid reaction mass. Optimization of the system involves providing the optimum relationship between the thickness of each reaction chamber, the loading density of reactant in the chambers, and the chamber depth, (diffusion length from gas passage to furthestmost reactant). Spacing between plates or other barriers is adjusted as required to optimize thermal conduction path lengths and give proper system thermal conductance. In the systems utilizing the improvement of the invention, solid is maintained at densities (based on solid reactant mass) typically between 0.2 and 2.5 g/cc.

In Figs. 1 and 2 there are illustrated a first means for restricting the solid reactant composition 20 which has been placed in a series of reaction chambers defined between heat transfer plates 12 mounted along heat transfer tube 14. The plates are shown as being annular in shape, although any suitable shape may be used as may the cross-sectional shape of the heat transfer tube to which they are secured. Around the outside of the reactor is a wire mesh 10 which provides free movement of the gaseous reactants to and from the solid reactant material as well as restraining expansion of the solid reactant within each of the reaction chambers. The heat transfer plates also provide for heat transfer to and from the solid reactant material and the heat transfer tubes. A suitable heat exchange fluid passes along the interior 16 of heat transfer tube 14.

The wire mesh is only one example of a volumetric expansion barrier which is porous or otherwise provides a path for the gaseous reactants. Typical mesh size will be

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about 250, although larger or smaller mesh may also be used. The particle size of the solid reactant is not so important, and it has been found that even particles that are smaller than the wire mesh opening size do not create a problem since the expansion barrier will be effective once the chemisorption reactions begin as the solid reaction mass will become somewhat stiffened. The solid complex compound is shown as substantially filling the reaction chambers as it will in an expanded condition. However, when initially charging a solid complex forming salt into the apparatus, particularly with substantially expanding solids it is usually preferred to charge the reaction chambers to less than full chamber volume, for example 40%-90%, thereby leaving some space for solid expansion. The invention also contemplates means for moving the reactor bed plates and/or the wire mesh to create reaction chambers having variable volumes to compensate for solid expansion and contraction as will be explained in more detail hereinafter.

Tests using the apparatus of Fig. 1 with SrCl_2 loaded into the reactor chamber at densities of 0.6 g/cc have given ammonia adsorption rates as high as 18 moles ammonia/mole SrCl_2 per hour initially, with average rates of 8-12 moles/mole after 15 minutes. Comparable tests without density control gives rates of about 2 to 5 moles/mole-hr. Similar results have been obtained with CaCl_2 , CaBr_2 , CoCl_2 , MgBr_2 , MgCl_2 , NaBr , SnCl_2 , BaCl_2 , MnCl_2 , MnBr_2 , NiCl_2 , SrBr_2 , and ZnCl_2 activated carbon, and Na-zeolite.

In Figs. 3 and 4 there is illustrated another example of a chemisorption reaction system in which the reaction chambers are located within one or more elongated sleeves or reaction columns 30. Within the column are a plurality of stacked reaction chambers each containing a suitable amount of solid reactant 34 on reactant support trays 32. These support trays are secured to column 30 which allows the heat transfer from the complex compound to

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and from the reactant support trays to the column and refrigerant fluid. The gaseous reactant is diffused into the solid reactant 34 via perforated tube 36 which restrains the solid reactant from excess volumetric expansion within the reaction chambers. Again, other suitable means such as a wire mesh, foam, pumice or other porous means which allow the gaseous reactants to move to and from the reaction chambers may be substituted for the perforated tube 36.

The shape of the heat transfer column 30 and the reactant support trays 32 is not critical. It should also be appreciated that the depth or dimension of the reaction chambers may be varied to obtain optimum thickness, depending on the type of reactant used and the density of the complex compounds being used. Reactant layer thickness typically varies from over 1" to 0.05". Thin layers usually provide better heat transfer and increasing reaction rates, but returns diminish at very thin layers because diffusion becomes limiting and heat transfer no longer controls the reaction rate. Optimal thickness is a function of reactant properties. Thus, deeper reaction chambers may be preferred for some sorption reactions since it will maximize the ratio of solid reactant mass to the total mass of the system by utilizing fewer reaction chambers, fewer reactant support trays, thereby further decreasing reaction vessel costs and weight. Moreover, where reaction chamber space is increased to provide a concomitant increase in the amount of solid reactant used in the reactant vessel, the free volume of gaseous reactant is also minimized or reduced. This advantage is further enhanced since the limitation of the volumetric expansion of the solid complex compound reduces the porosity of the solid reactant thereby minimizing the amount of free gas used. Such gas utilization reduction is important for cyclic processes in which temperature and pressure vary, because energy is consumed in heating/cooling and/or compressing or expanding free gas with

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additional energy use or loss thereby effecting the efficiency of the overall system operation.

Another reactor configuration is illustrated in Figs. 5 and 6 in which heat transfer conduits 42 extend through a plurality of reactant support trays 40 which are supported on the heat transfer conduits. Again, a suitable heat exchange fluid will pass through the heat transfer tubes to take advantage of the alternate heating and cooling caused by the chemisorption reaction occurring as the gaseous reactant is alternately adsorbed and desorbed from the solid reaction mass. Solid reactant 44 is illustrated in the plurality of reaction chambers located between the reactant support trays, with a wire mesh volumetric expansion barrier 45 secured around the exterior of the reactant support trays.

Figs. 7 and 8 illustrate yet another embodiment similar to that of Figs. 1 and 2 but incorporating a porous sleeve 46 which surrounds heat transfer tube 47 to allow gaseous reactant to have access to solid reactant 49 from both the inside and outside periphery. Larger overall diameters can be used because the diffusion path is reduced by a factor of two. Wire screen 48 surrounds the solid reactant column. Although a plurality of reactant support trays are shown in Figs. 1-8, only an upper and lower end plates may be used, with the solid reactant formed in a column therebetween and encased within the wire mesh. Alternatively, any number of trays may be used along the column.

In Fig. 9 there is schematically illustrated yet another embodiment of the invention incorporating a wire mesh support screen 50 secured entirely around a heat exchanger 56 to create upper and lower reaction chambers. These reaction chambers are initially partially or completely filled with solid reactant 52 and 54, respectively, depending on the solid expansion, so that each

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reaction chamber is defined between the wire support screens 50 and the surface of the heat exchanger. The heat exchanger illustrated is shown from a side view so that the heat exchanger is viewed along its narrow component and having relatively wide upper and lower surfaces 51 and 55, respectively. The heat exchanger may also be circular or shaped differently and the specific shape is not particularly critical. It is to be understood that the heat exchange surface exposed to the solid reactant may be configured to maximize heat exchange efficiency to and from the solid reactant. An advantage of the design of this embodiment is the relatively large surface area of the solid reactant exposed to a gaseous reactant. Again, other materials which will restrict volumetric expansion and at the same time offer suitable gaseous movement to and from the reaction chambers and solid reactant may be used. A suitable heat exchange fluid will be transmitted via pipes 57 and 59 to and from the heat exchanger 56. The thickness of the solid reactant layers can be varied to achieve a desired gas diffusion path length.

In Fig. 10 wire mesh 62 or other similar porous material for restraining the volumetric increase of solid reactants 65 is shown. In this embodiment, the perforated or mesh volume restriction member is on the outside of the plurality of reaction chambers in which a plurality of heat exchange plates 61, similar to that shown in Fig. 9, are positioned. Thus, the exterior or outside reaction chambers have the advantage of the relatively large solid surface exposed to the gaseous reactant with the interior reaction chambers being more limited with only their ends being exposed. However, the heat exchangers may have any suitable shape, including curved or otherwise differently shaped surfaces for taking advantage of the solid reactant to which each is exposed.

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Figs. 11 and 12 illustrate yet another embodiment in which volume restraining wire mesh 72 surrounds a column of solid reactant 76 supported around a plurality of heat exchange fins 74 extending radially from heat transfer tube or conduit 75. In Fig. 12, the fins not in the cross-section plane are shown with a phantom or hidden line. The length, shape and number of such heat exchange fins or their equivalent, may be selected to suit the particular needs of the apparatus and its intended function and performance requirements. The solid reactant column may be used in a heat exchange reactor in which the solid reactant alternately adsorbs and desorbs gaseous reactant. In such a reactor the open space may be flooded with suitable gaseous ligand which would then be adsorbed on the solid reactant. The components and features of such a gaseous-solid thermal system are known to those skilled in the art and are not explained in any further detail herein, not being part of the invention.

Figs. 13-17 illustrate the improvement of the invention showing a comparison between various complex compounds during adsorption or desorption when allowed to expand freely and when the expansion is limited according to the invention. In the examples as shown, each of the adsorbents is placed in an apparatus as shown in Figs. 1 and 2 whereby the expansion is restricted during the adsorption or desorption process. The salts as shown are complexed with ammonia ligand which is adsorbed or desorbed from the complex between the moles of ligand shown after the salt. Thus, in Fig. 13, $\text{CaCl}_2 \cdot 8\text{NH}_3$ is desorbed to $\text{CaCl}_2 \cdot 4\text{NH}_3$ with the heat transfer fluid temperature in the apparatus at 45°C , and the pressure in the reaction vessel at 1.37 Bar. The reaction rate is shown in moles of ammonia per mole of salt per hour. The graphs show clearly the improvement of the invention over free expansion of salts with significant improvement in reaction rates being achieved.

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In another embodiment of the invention the reaction chamber volume is variable in the walls, trays and/or other components defining the chamber are movable. For example, the reactant trays may be free to move up and down along the heat transfer tube. Thus, in this embodiment, in the apparatus shown in Figs. 1-8, the reactant support plates, are free to slide upwardly or downwardly along the heat transfer tube, gravitationally biased or urged toward one another when the tube is in a vertical or upright position. With the reactant solid between the trays, the trays are urged together against the solid to maintain a constant force and compression both during expansion and contraction. The wire mesh or other porous restraining means may also be slidable or movable in the apparatus. The reaction plates and/or the wire mesh may also be biased utilizing springs or other biasing means. Thus, in this embodiment, observing Figs. 1-11, the wire mesh screen is biased such that it is urged and compressed against the solid reactant in the reaction chambers. Such a feature provides for automatically varying the reaction chamber volume as the reacting solids expand and contract. Such a movable reactor support and/or porous volume restraining means feature may be incorporated in any of the apparatus shown and described herein. This embodiment may be used with complex compounds having substantial expansion as previously described. However, the embodiment is also particularly useful where the reacting solids do not undergo substantial expansion, for example, certain metal hydrides and oxides and particularly zeolites, activated carbon and silica gel.

In another embodiment of the invention, optimum reaction density of a solid reactant is maintained in a reaction chamber having a fixed volume by mixing the solid reactant with a solid material which is inert to both the solid reactant and gaseous reactant at the chemisorption reaction conditions. The inert solid materials mixed with

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the solid reactants are preferably porous or particulate and of high thermal conductivity. With such properties, these additives allow for movement of the gaseous ligand reactants to and from the solid reactants, as well as to provide for heat transfer to and from the solid reactants and complex compounds in the reaction chambers as previously described. For this purpose, examples of suitable materials include $\text{CaCl}_2 \cdot 2\text{NH}_3$, aluminum wool, porous metal granulates, alumina-silica solids, and the like. Such examples are not intended to be limiting in any way, and any porous and highly thermal conductive solid which is inert to the reactants as previously described in the chemisorption process conditions for example, temperature ranges between about -65°C to about 1000°C and pressures of between about .001 and about 150 atmospheres may be used. The amount of inert solid material will depend on the particular solid reactant being used, as well as the particle size of the solid reactant and inert material. However, for most reactions, the amount of inert solid material between about 1 and about 60%, by weight of the mixture, will be suitable.

In using the mixture of the inert solid material and solid reactant, the reaction chamber may be partially or totally filled. However, where the chamber is partially filled, the amount of mixture will be such that when the solid mixture expands due to the formation of the complex compound, expansion will be limited by the volume of the reaction chamber. Thus, the volume of mixture used, even if less than the fixed volume of the reaction chamber will be such that the expanded solid reaction mixture would be greater than the volume of the reaction chamber if the reaction was carried out without volumetric restriction to the solid reactant. With such a system, one skilled in the art may select the optimum density of the solid reactant desired to be maintained during the chemisorption reaction, and select the amount of inert material to be mixed as well

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as the desired volumes of the solid mixture to be introduced into the fixed volume reaction chamber.

5 The improvement and advantages achieved utilizing a system and method employing solid-gas reactions as disclosed herein include industrial processing, and especially in cyclic processing in which the solid reactant is not consumed, but is continually regenerated in the alternating adsorption-desorption reactions. These processes include pressure swing and temperature swing adsorption reactions
10 for separating gases, recovery of solvents from gas streams, removal of contaminants, adsorption heat pumps, thermal storage systems, refrigerators, and the like. The invention provides for decreased cost and higher reaction rates because of the substantially increased thermal conductivity
15 at high density and ability to achieve optimum solid reactant porosity and thermal conductivity. Low cost and efficiency is further achieved by use of extended heat transfer surfaces as reactant support plates, thus providing short thermal paths through the solid reactant at low cost.

20 In systems in which the initial state of the solid reactant has excessive porosity, particularly the inclusion compounds such as zeolites, activated carbons and silica gel, the reactant is compressed to the optimum density in the reaction chamber at the time of loading and held to that
25 density by the volume restricting means. Thus, when loading the inclusion compounds, or other solids having little or no volumetric expansion, they are introduced into the reaction chamber space and compressed, for example up to 20%, or more of their uncompressed or pour density. Such solids are also
30 loaded into the reaction chamber to substantially fill the chamber space. The invention also improves systems in which the initial state of the solid reactant mass is of insufficient porosity, whereby the reactant is decompressed, typically by particle size reduction, or with addition of
35 inert materials, and contained in the reactor at optimum

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density. In addition, because of compression of the reactant to optimum density against the heat transfer surface in each reaction chamber, improved heat transfer and thermal conductivity is achieved throughout the reactor.

5 Moreover, the systems incorporating the invention have higher reaction rates and provide greater heat flux at heat transfer surfaces, require minimum volume of gaseous reactant, and maximize the ratio of solid reactant mass to total reactor mass. Such advantages over prior art systems
10 yield lower cost per unit area supporting the solid reactant. These as well as other advantages of the invention will be evident to those skilled in the art as will various modifications, adaptations and features of apparatus components utilizing the concepts disclosed
15 herein.

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CLAIMS:

1. A method of increasing a reaction rate in a chemisorption reaction process in which a gaseous reactant is alternately adsorbed and desorbed on a solid reaction product
5 formed by adsorbing the gaseous reactant on a solid reactant, the reaction product having an increased or decreased volume as compared to the unreacted solid reactant,

wherein the reaction rate of the chemisorption reaction is increased by maintaining an optimized density of the solid
10 reaction product during the reaction by contacting the solid reactant and reaction product with a volumetric expansion control means during at least a portion of the chemisorption reaction whereby expansion of the solid reaction product is limited so as to improve the reaction rate of the process and
15 carrying out the chemisorption reaction process at the improved reaction rate using the said solid reaction product.

2. The method of claim 1, wherein the solid reactant comprises:

(a) a metal hydride, carbonate, halide, oxide sulfate, sulfite, nitrate, nitrite or oxalate in which the metal is an
20 alkali metal, alkaline earth metal, transition metal, aluminum or zinc;

(b) a double metal salt in which the two metals are selected from strontium, sodium, aluminum, silver, gold,
25 calcium, magnesium and cobalt;

(c) ammonium chloride; or

(d) a double metal salt in which one metal is an alkali or alkaline earth metal, and

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wherein the gaseous reactant comprises ammonia, water, carbon dioxide, sulfur dioxide, a lower alkanol, an alkyl amine, a polyamine or phosphine.

3. The method of claim 1 or 2, wherein the solid
5 reactant is introduced into one or more reaction chambers at a first, uncompressed density and compressed to a second density, greater than the first density, prior to the chemisorption reaction.

4. The method of claim 3, wherein the reaction product
10 is expanded to a third density, less than the second density, during the chemisorption reaction.

5. The method of any one of claims 1 to 4, wherein the
solid reactant is used as a mixture with a solid material inert to the solid reactant and the gaseous reactant in the
15 chemisorption reaction.

6. The method of any one of claims 1 to 5, wherein at
least a portion of the volumetric expansion control means has a heat transfer surface and the solid reactant and reaction
product are expanded or compressed against the heat transfer
20 surface during the reaction.

7. The method of any one of claims 1 to 6, wherein the
solid reactant is introduced into a reaction chamber at a density to provide for optimized relationship between gaseous
reactant diffusion and thermal conduction throughout the solid
25 reaction mass.

8. The method of any one of claims 1 to 7, wherein the
volumetric expansion control means is movable between a first position in which the reaction chambers in which the reaction
is carried out have a first volume and a second position in
30 which the reaction chambers have a second volume, greater than

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the first volume; the solid reactant is located into the reaction chambers at the first volume; and the solid and gaseous reactants are exposed to form the reaction product having a second volume.

5 9. The method of claim 1, wherein:

the solid reactant at a first uncompressed density is introduced into a reaction chamber having one or more movable barriers for varying the volume of the reaction chamber;

10 the solid reactant is compressed to a second density greater than the first density;

the reaction chamber is substantially filled with the solid reactant at the second density; and

15 the gaseous reactant is exposed to the solid reactant to form the reaction product while maintaining compression of the solid in the reaction chamber with the said one or more movable barriers.

10. The method of claim 5, wherein:

20 a mixture of the solid reactant and the inert solid material is introduced into one or more reaction chambers each having a first volume, the mixture being introduced to fill each of the reaction chambers to a second volume, less than or equal to the first volume, and

25 the gaseous reactant is exposed to the solid reactant to form the reaction product at a second density, greater than the first density.

11. A reaction apparatus comprising:

one or more reaction chambers for containing a solid reactant and a gaseous reactant exposed to the solid reactant

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and for reacting therewith to form a solid reaction product having an increased or decreased volume as compared to the volume as compared to the volume of the solid reactant prior to the reaction; and

5 movable volumetric expansion control means for contacting the solid reactant and the reaction product and optimizing the density thereof during the reaction by limiting the volumetric expansion thereof.

12. Apparatus of claim 11, wherein at least a portion of
10 the volumetric expansion control means comprises a heat transfer surface for exchange of heat with the solid reactant during the reaction.

13. Apparatus of claim 11, wherein the geometry of the reaction chambers provides for optimized relationship between gaseous reactant diffusion path length and thermal conduction path length throughout the solid reaction mass.

14. Apparatus of claim 11, wherein at least a portion of the reaction chambers include a heat exchange surface member extending from a wall of a heat exchange fluid conduit.

15. Apparatus of claim 11, wherein at least a portion of the reaction chambers include a surface of a heat exchange fluid conduit exposed therein.

16. The apparatus of claim 11, wherein the volumetric expansion control means comprises a movable reactant support surface.

17. The apparatus of claim 16, wherein the reactant support surface is biased for being urged against the solid reactant and reaction product during the reaction.

18. The apparatus of claim 11, wherein the volumetric expansion control means comprises a porous wall for allowing the gaseous reactant to pass to and from the solid.

19. The apparatus of claim 18, wherein the porous wall is movable for varying the volume of the reaction chamber.

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20. The apparatus of claim 19, wherein the moveable porous wall is biased and urged against the solid reactant and reaction product during the reaction.

21. A method of increasing a reaction rate in a
5 chemisorption reaction process, wherein a gaseous reactant is alternately adsorbed and desorbed on a complex compound formed by adsorbing the gaseous reactant on a solid reactant, the complex compound having a first density when allowed to expand without restriction during the adsorption, which method
10 comprises:

maintaining the density of the complex compound during the reaction process at a second density greater than the first density whereby the reaction rate at which the gaseous reactant is capable of being adsorbed and desorbed on the complex
15 compound is increased as compared to a reaction rate using a complex compound formed without maintaining the density during the reaction, and

carrying out the chemisorption reaction process at the increased reaction rate using the complex compound formed by
20 maintaining the density during the reaction process.

22. The method of claim 21, wherein the second density is maintained by restricting the volumetric expansion of the complex compound during the chemisorption reaction.

23. The method of claim 21, wherein:

25 the solid reactant is mixed with a solid material inert to the solid reactant and the gaseous reactant under conditions of the chemisorption reaction;

the mixture of the solid reactant and the inert solid material is introduced into one or more reaction chambers each

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having a first volume to fill each of the reaction chambers to a second volume, less than or equal to the first volume; and

the gaseous reactant is exposed to the solid reactant to form the complex compound and the volumetric expansion of the complex compound is restricted during the reaction whereby the complex compound formed has a density greater than the density of the solid reactant prior to the reaction.

24. The method of any one of claims 1 to 10 or any one of claims 21 to 23, wherein the reaction rate increase comprises an increase in the number of mols of the gaseous reactant adsorbed and/or desorbed per mol of the solid reactant per hour at adsorption or desorption times of up to about 15 minutes.

25. The method of any one of claims 1 to 10 or any one of claims 21 to 23, wherein the reaction rate increase comprises an increase in the number of moles of the gaseous reactant adsorbed and/or desorbed per mol of the solid reactant per hour at adsorption or desorption times of less than 60 minutes respectively.

26. The method of any one of claims 1 to 10 or any one of claims 21 to 25, wherein the reaction product is a reaction product of ammonia with a salt selected from the group consisting of SrCl_2 , CaCl_2 , CaBr_2 , CoCl_2 , MgBr_2 , MgCl_2 , NaBr , SnCl_2 , BaCl_2 , MnCl_2 , MnBr_2 , NiCl_2 , SrBr_2 and ZnCl_2 .

27. The method of any one of claims 1 to 10 or any one of claims 21 to 25, wherein the gaseous reactant is ammonia and the solid reactant is SrCl_2 , CaCl_2 , MgCl_2 or CoCl_2 .

28. The method of any one of claims 1 to 10 or any one of claims 21 to 27, wherein the solid reactant is particulate.

29. The method of any one of claims 1 to 10 or any one of claims 21 to 28, wherein the volumetric expansion control means

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is a wire mesh, a perforated plate or tubing or a foam porous to gas; and is provided on at least one wall or barrier defining and surrounding a reaction chamber in which the chemisorption reaction takes place, while the remainder of the
5 reaction chamber is a heat exchange surface of a conduit for a heat exchange fluid.

30. The method of claim 29, wherein the chemisorption reaction takes place in a reactor which comprises (i) a series of reaction chambers defined between horizontal heat transfer
10 plates mounted along a central upright heat transfer tube and (ii) a wire mesh around an outside of the reactor.

31. The method of claim 28 or 29, wherein the chemisorption reaction is carried out using the apparatus of any one of claims 11 to 20.

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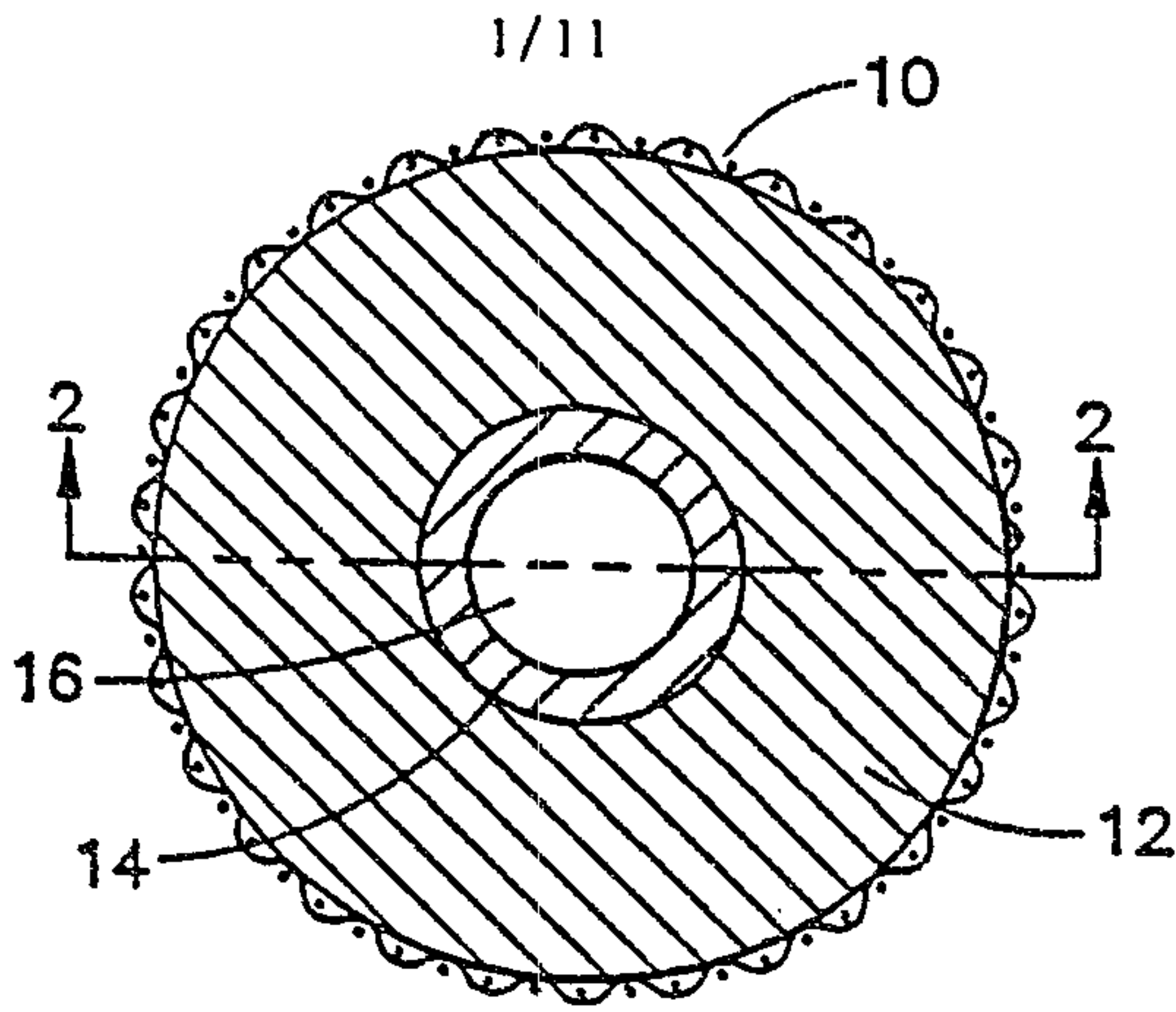


FIG. 1

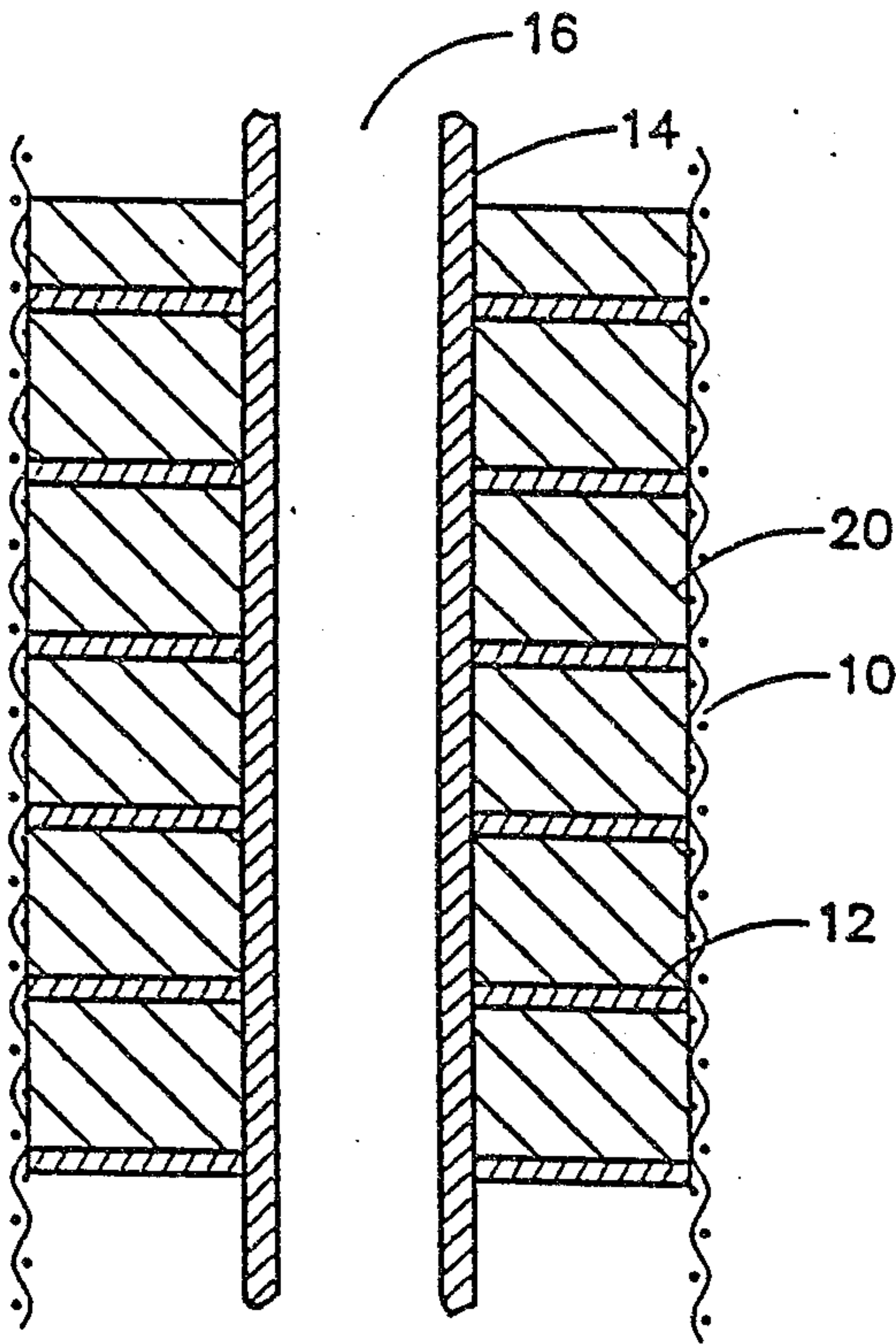


FIG. 2

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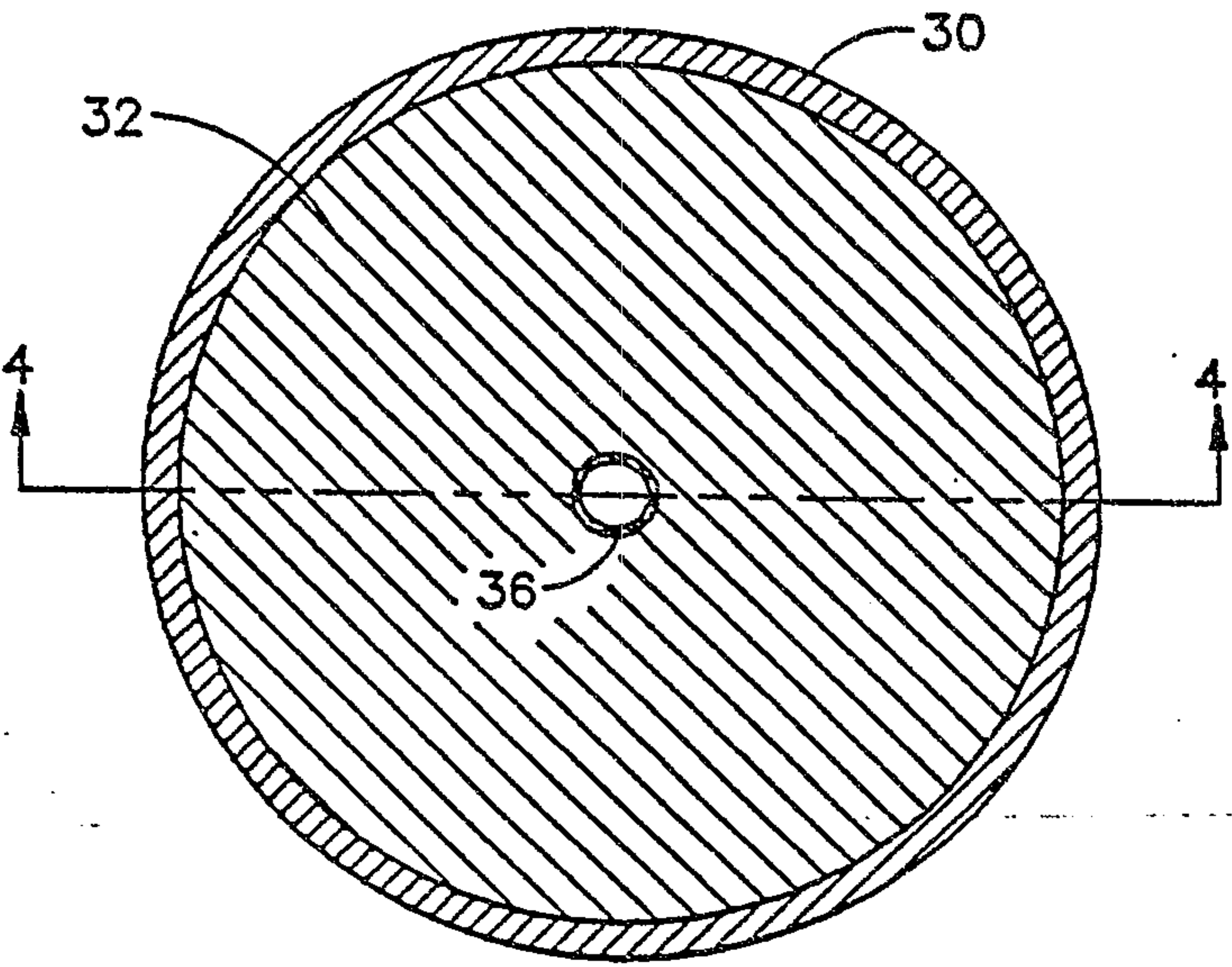


FIG. 3

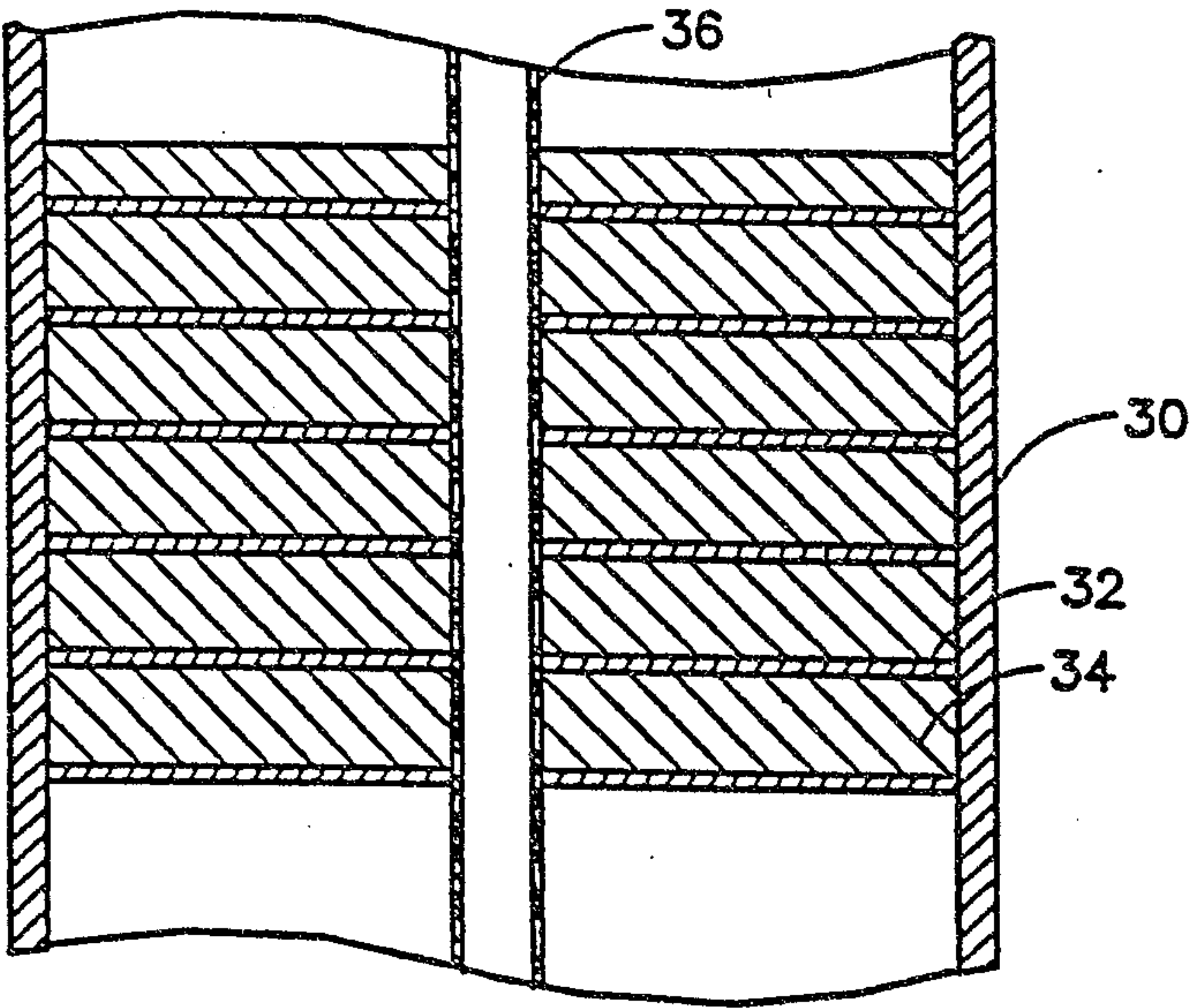


FIG. 4

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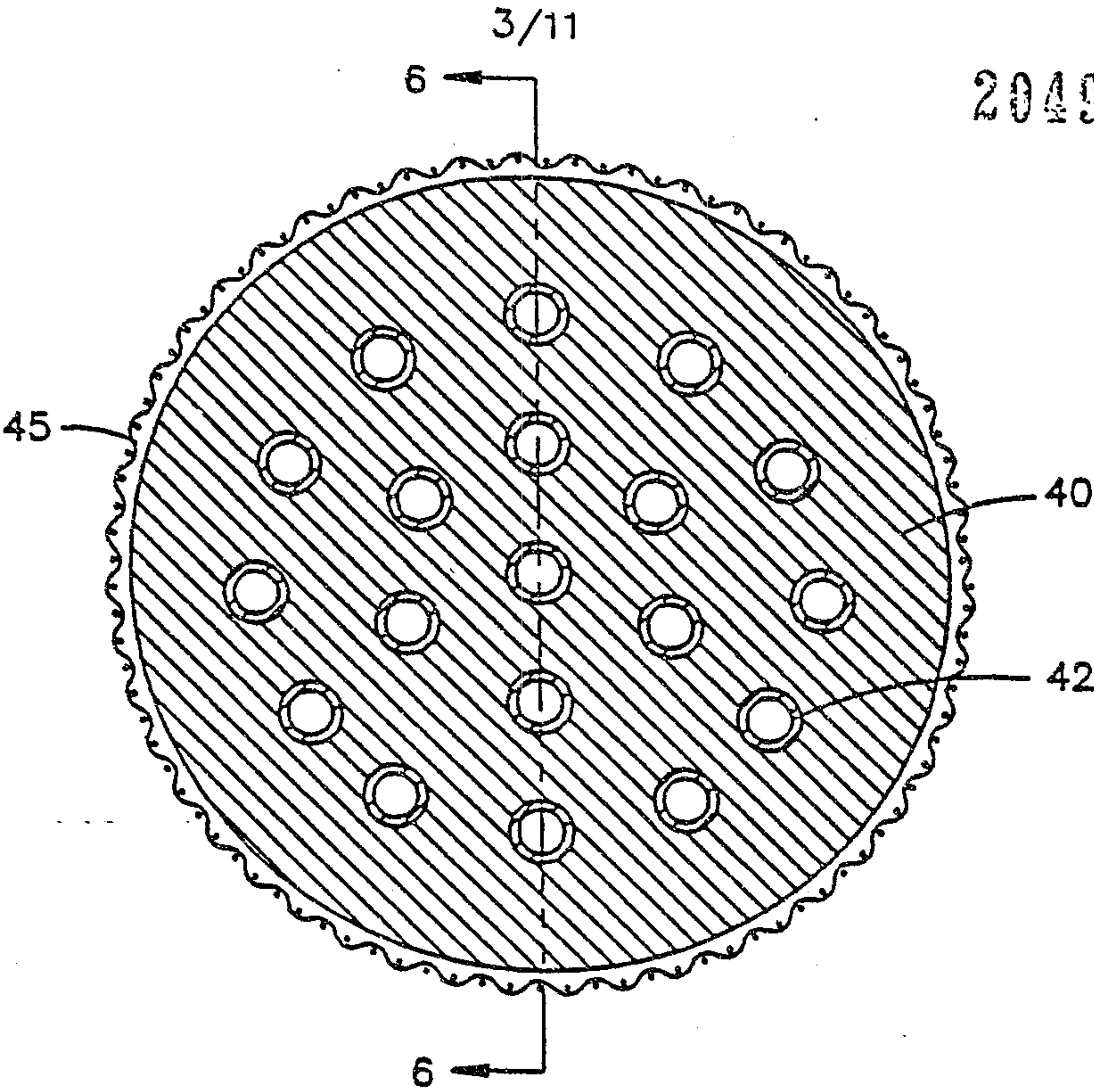


FIG. 5

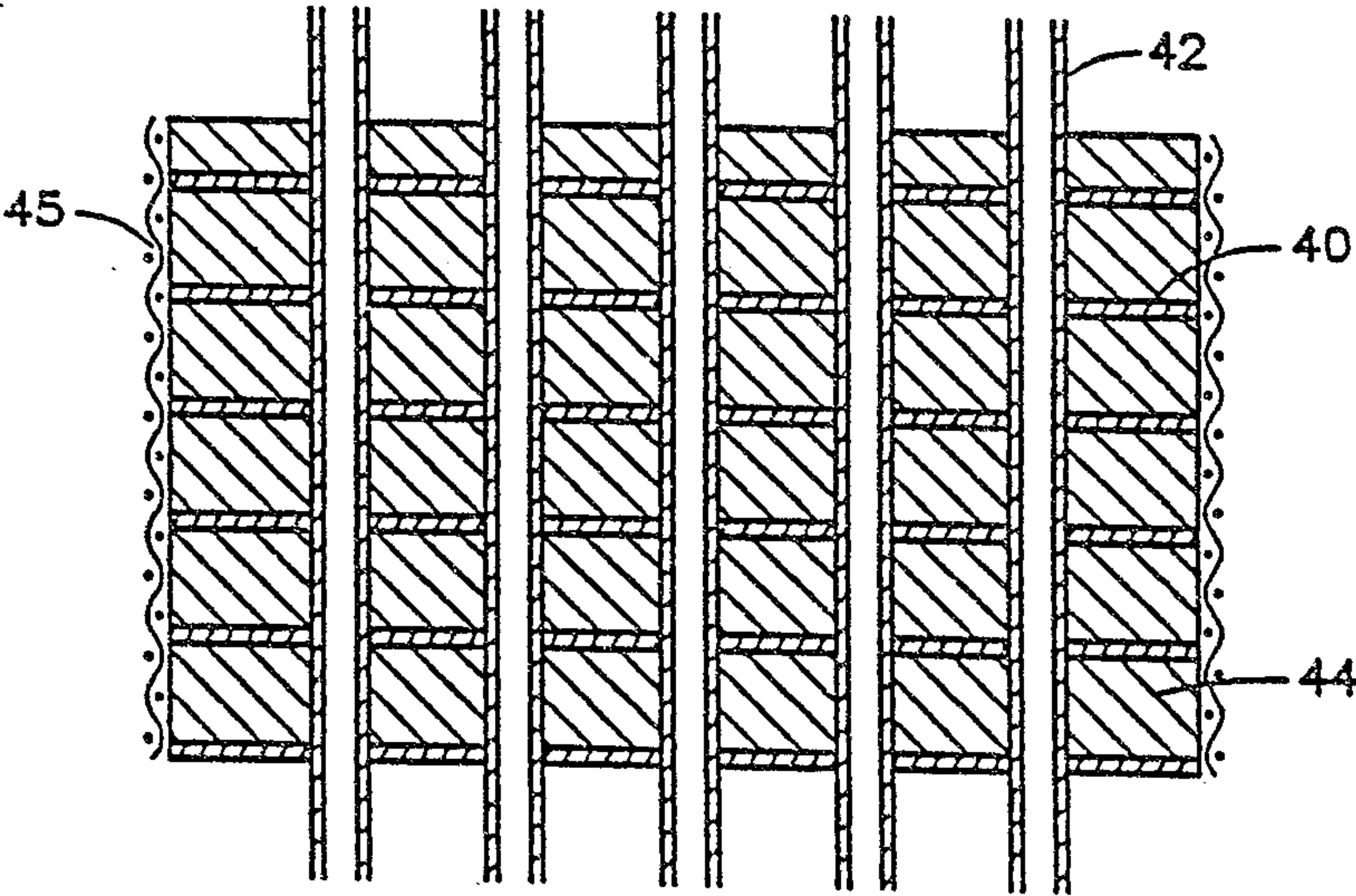


FIG. 6

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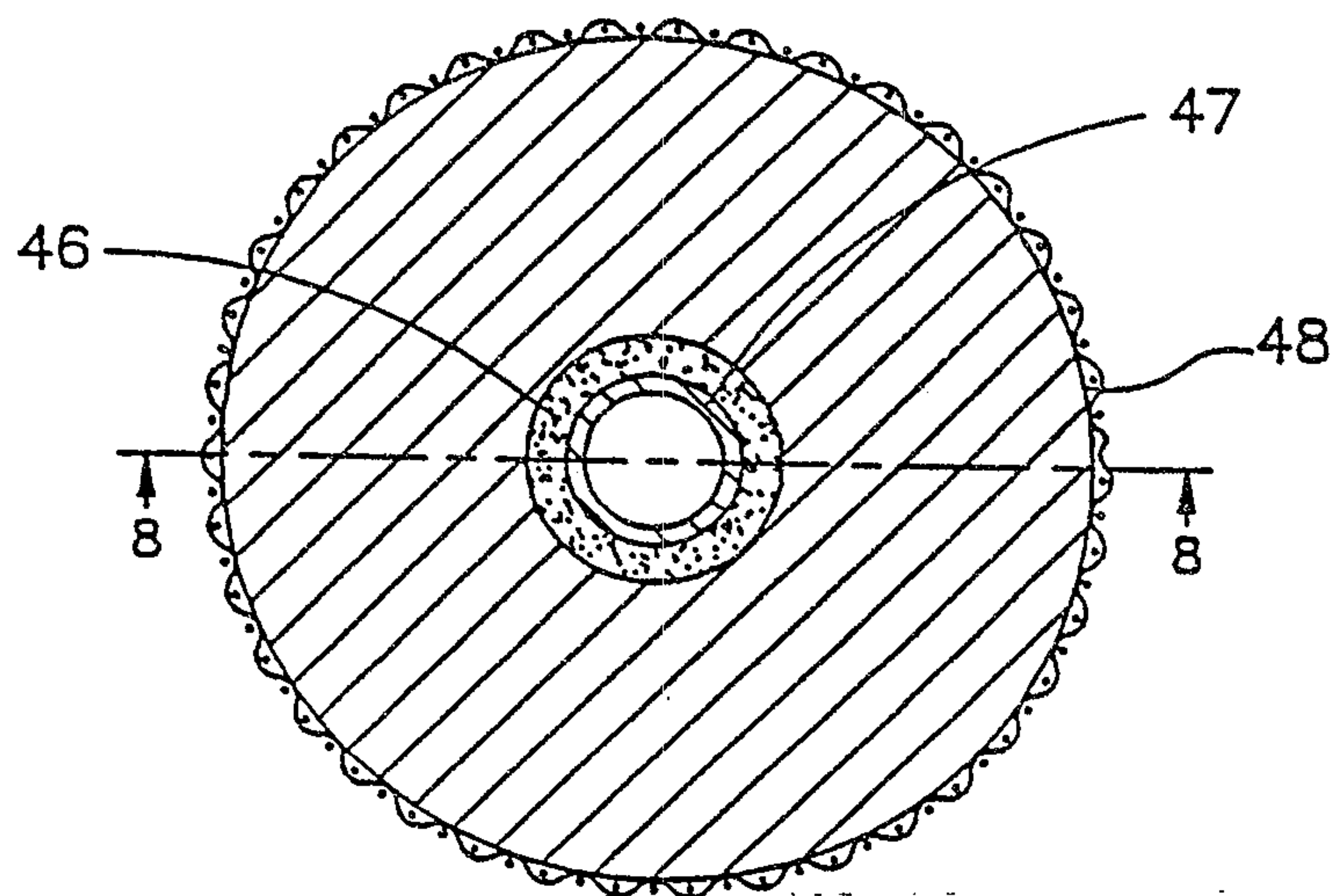


FIG. 7

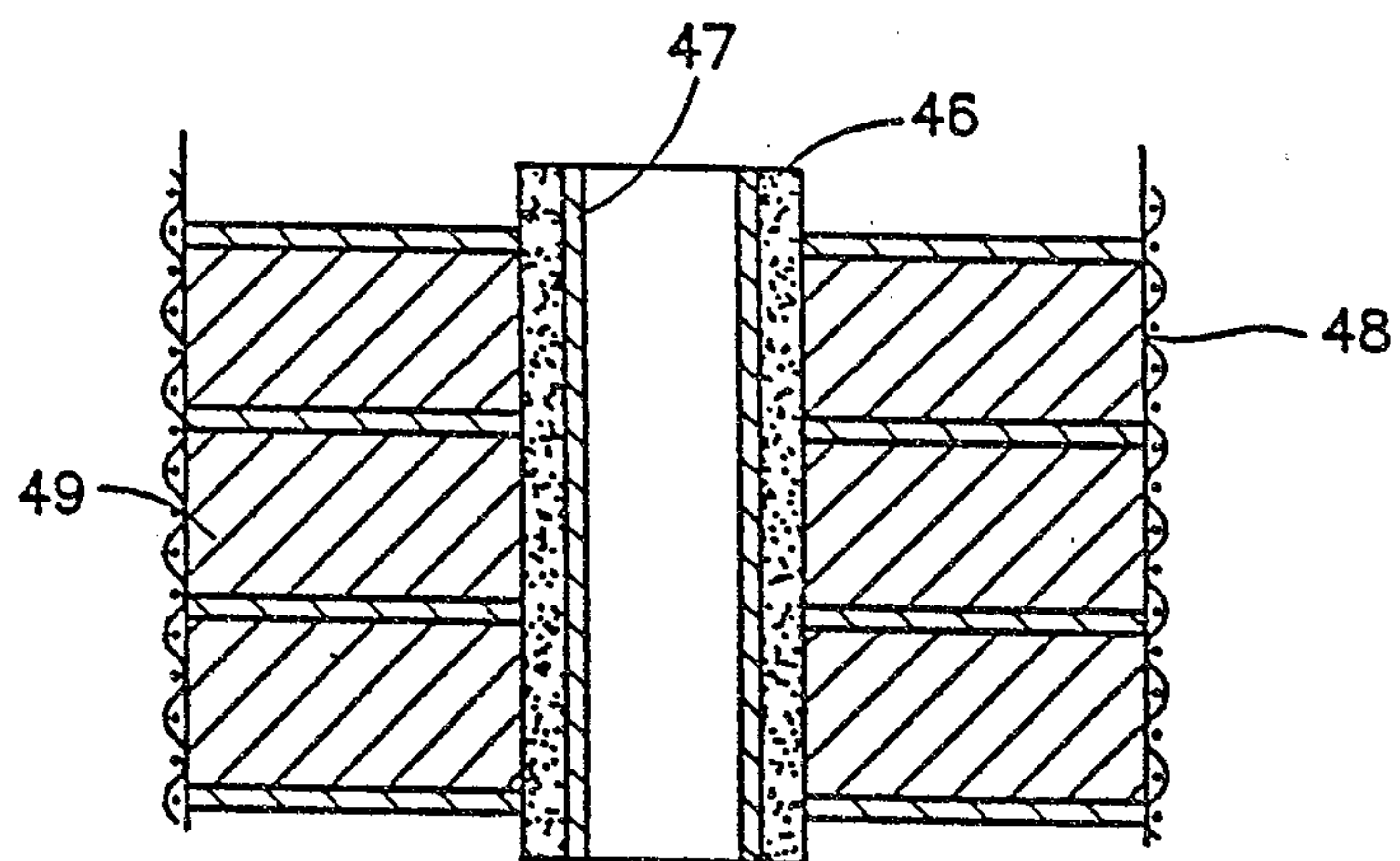


FIG. 8

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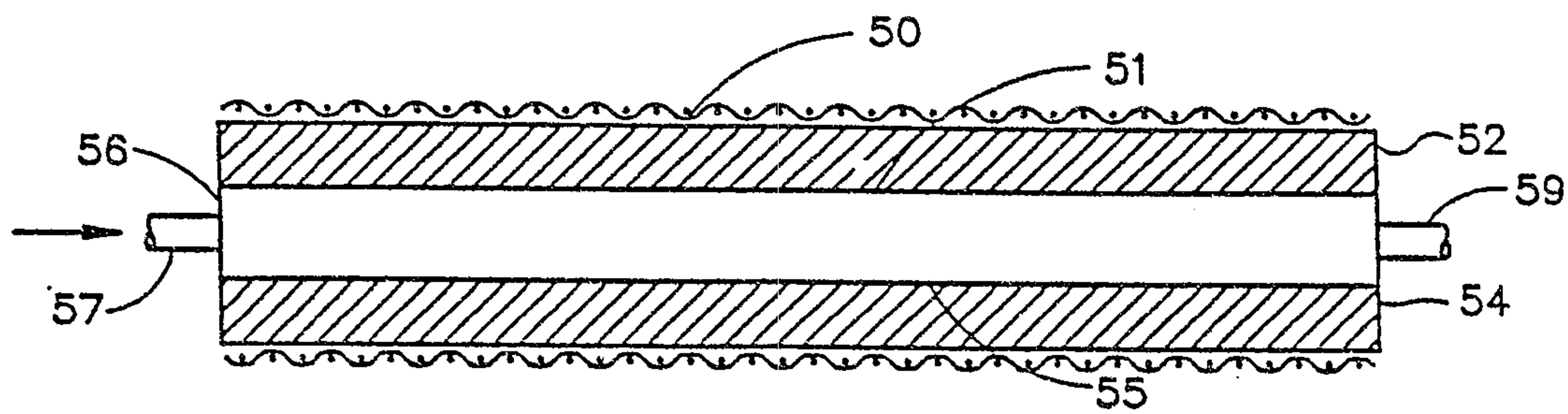


FIG. 9

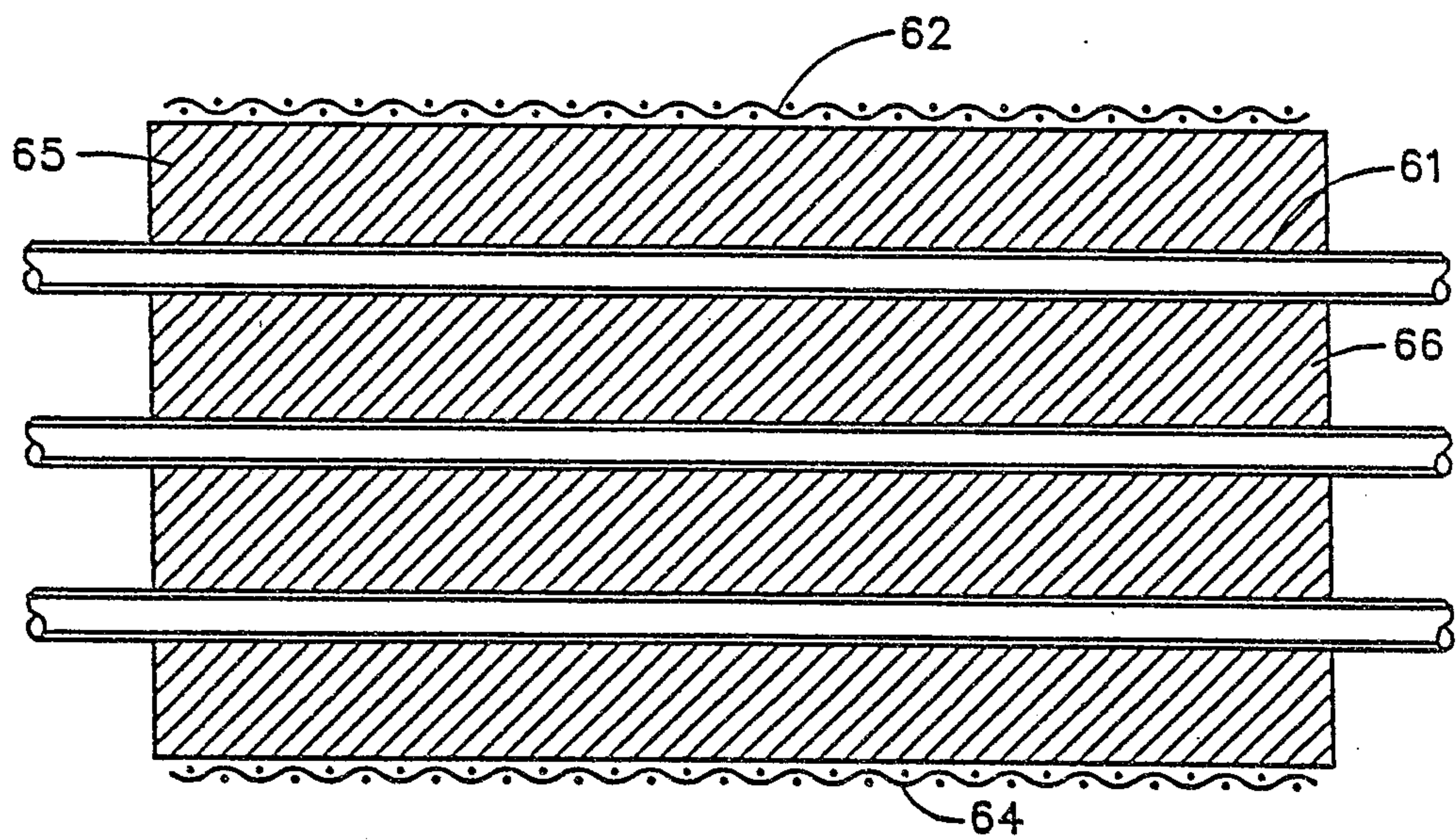


FIG. 10

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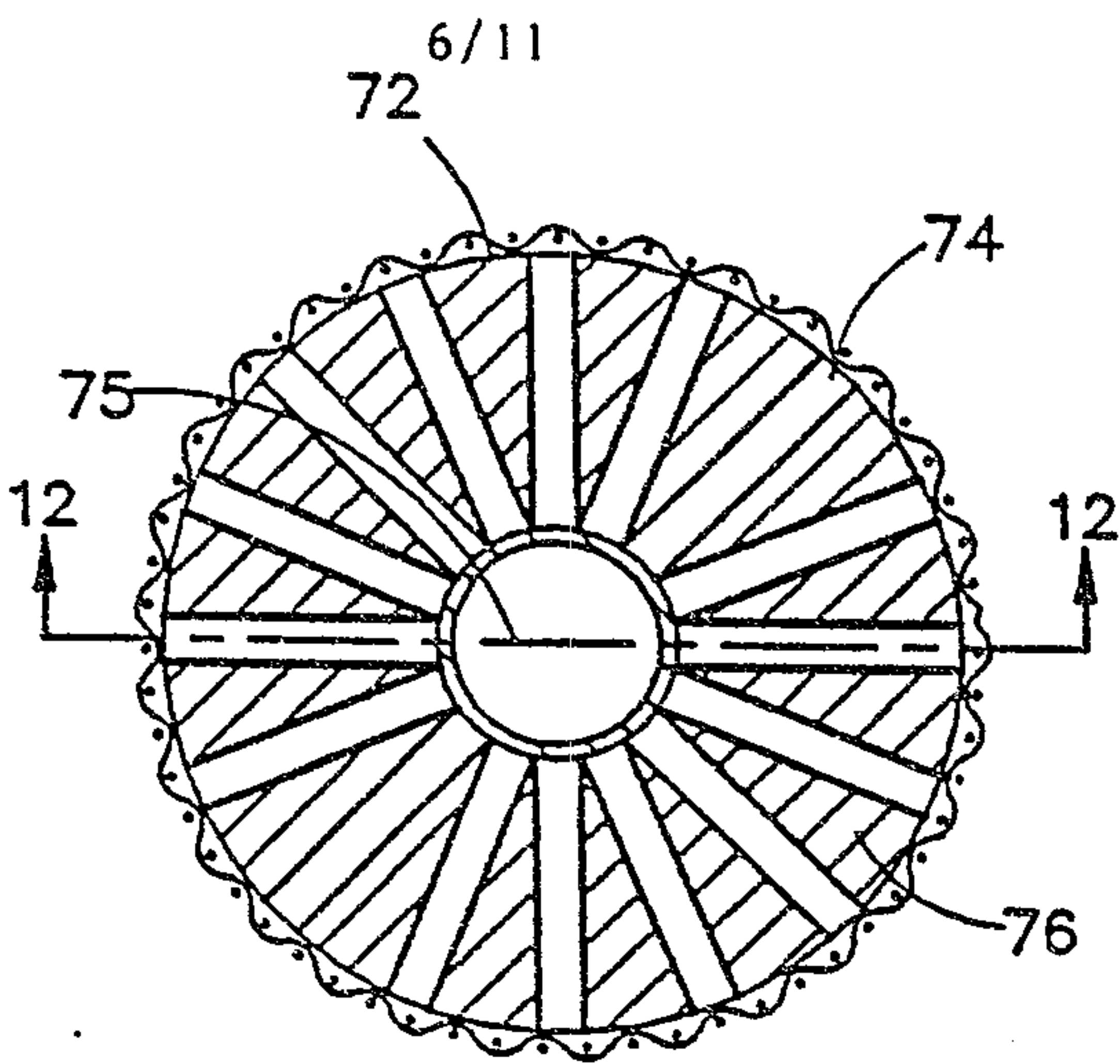


FIG. 11

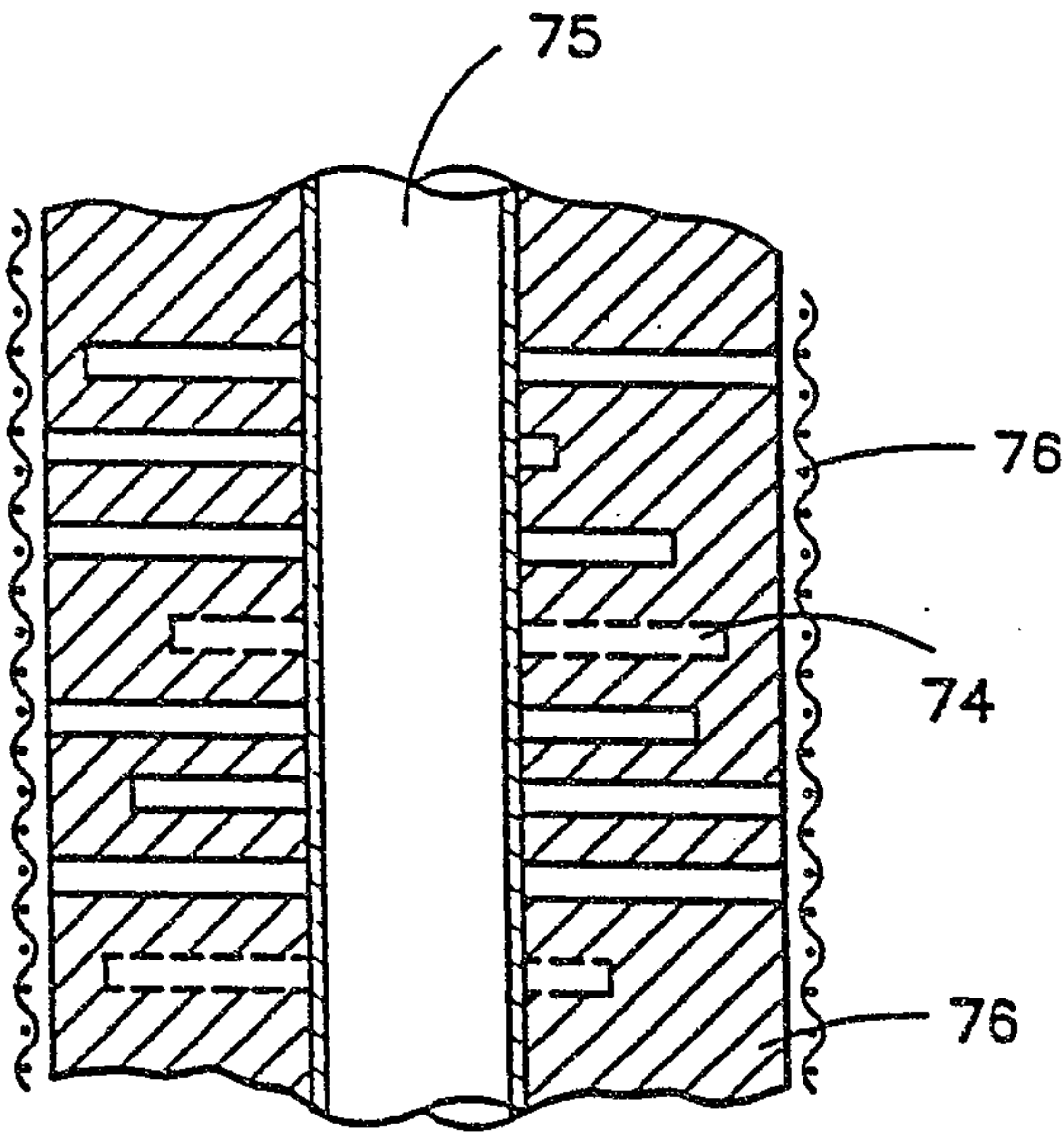


FIG. 12

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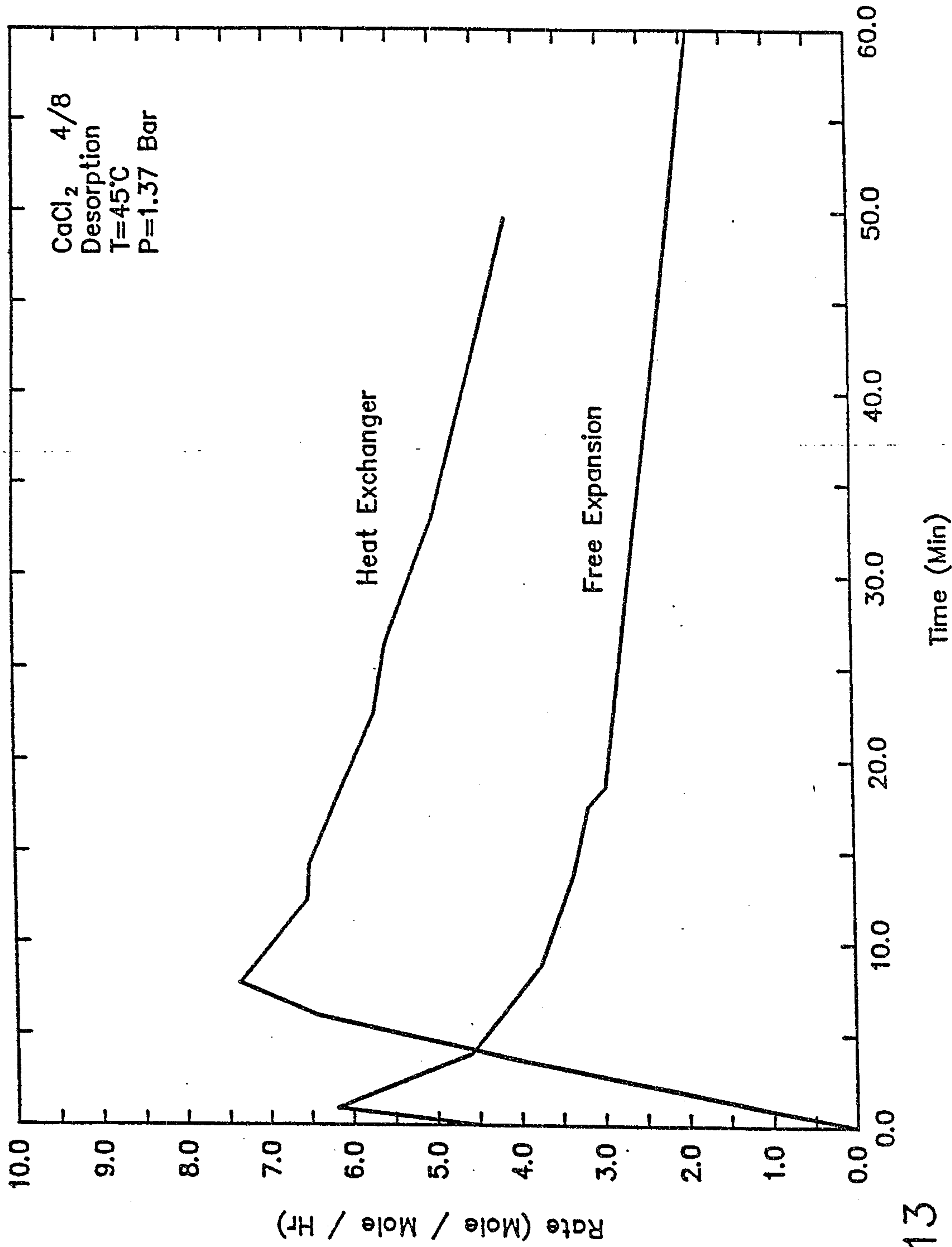


FIG. 13

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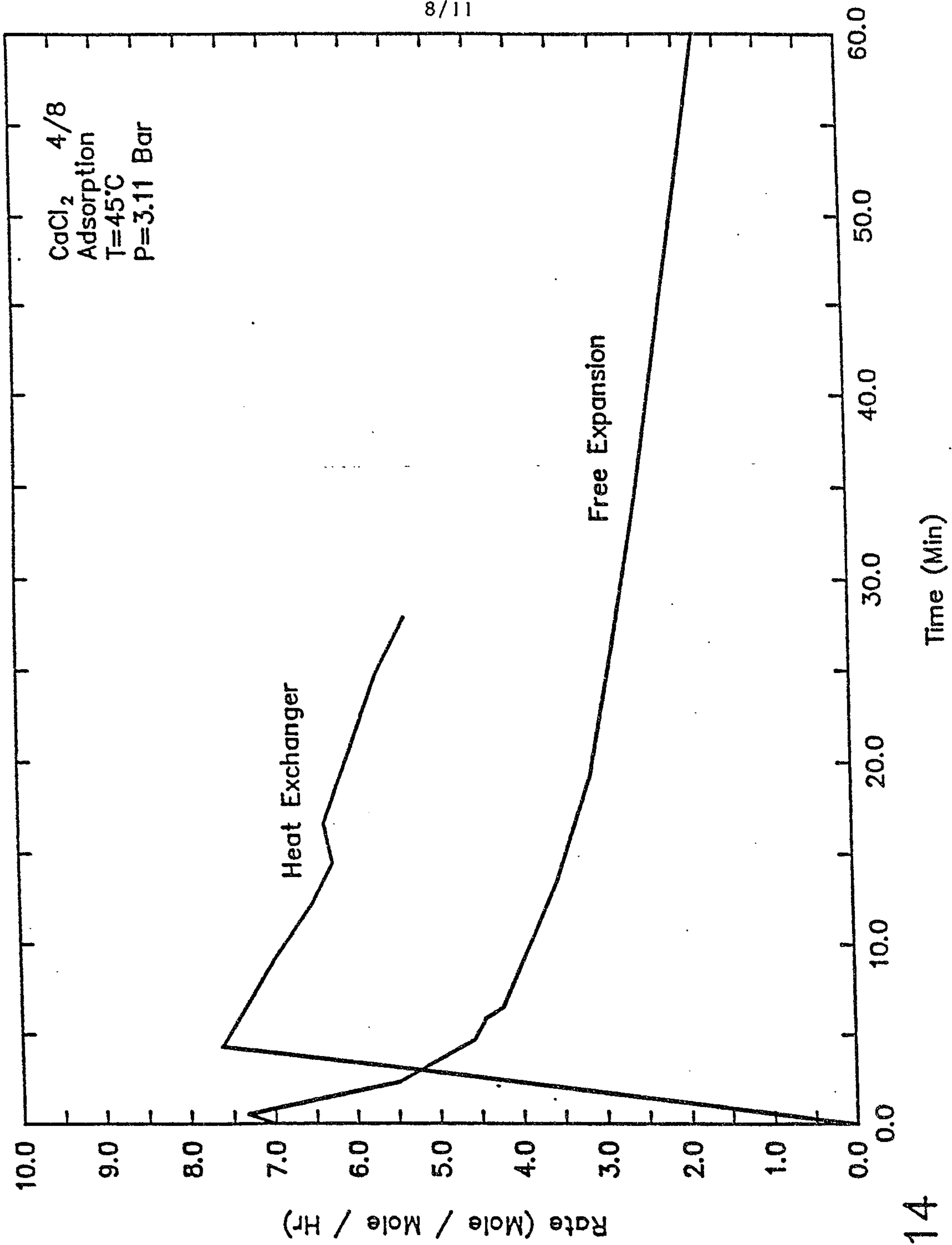


FIG. 14

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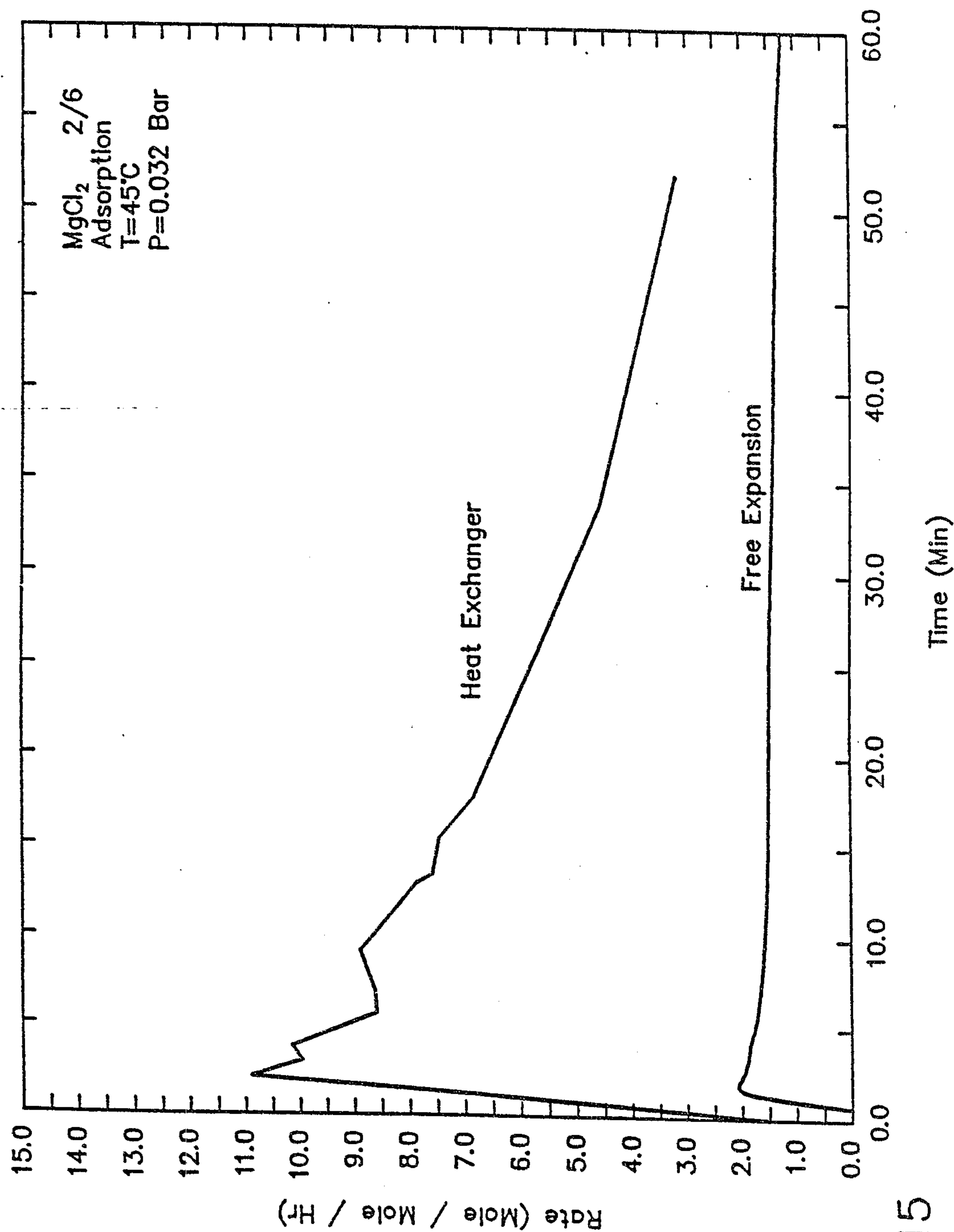


FIG. 15

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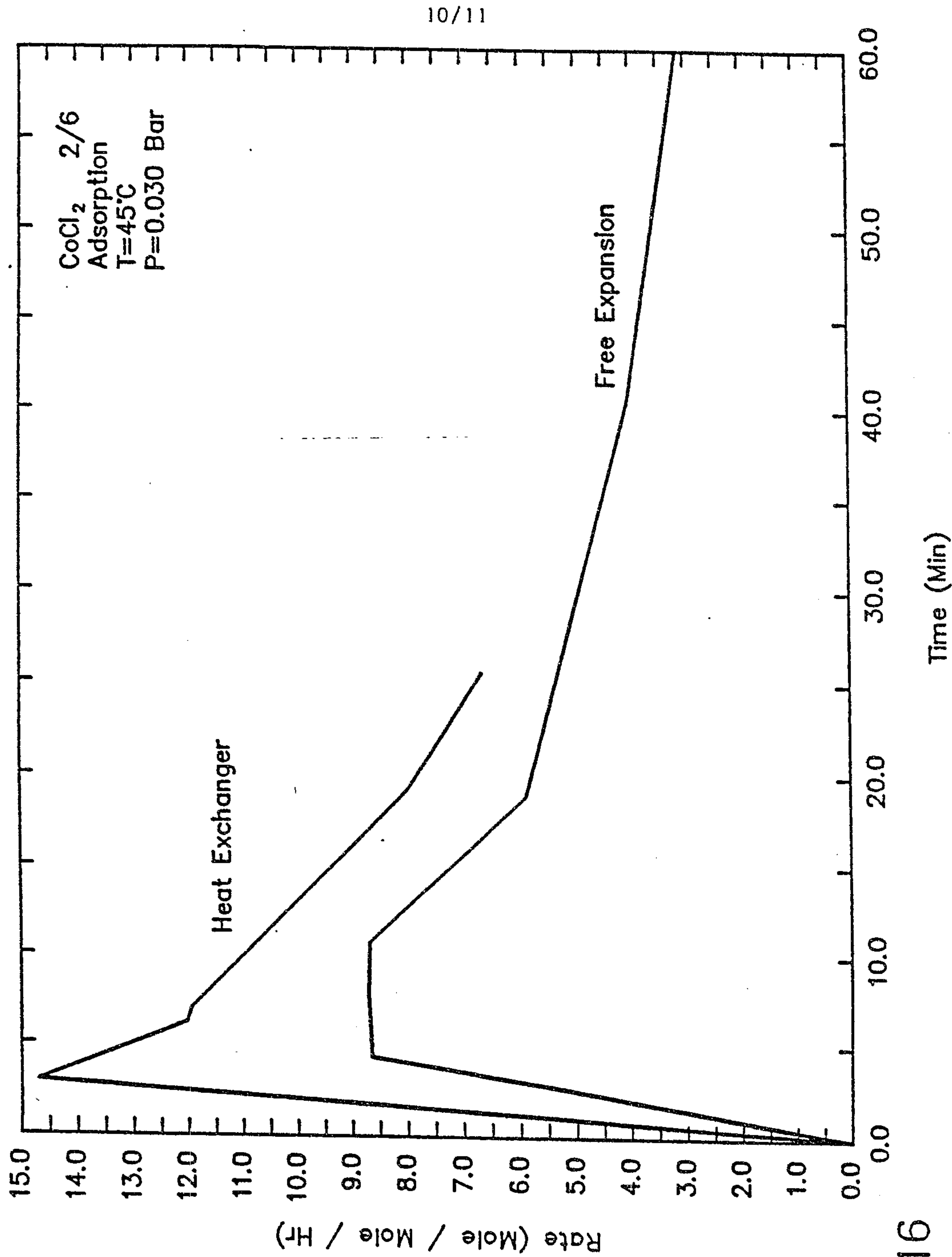


FIG. 16

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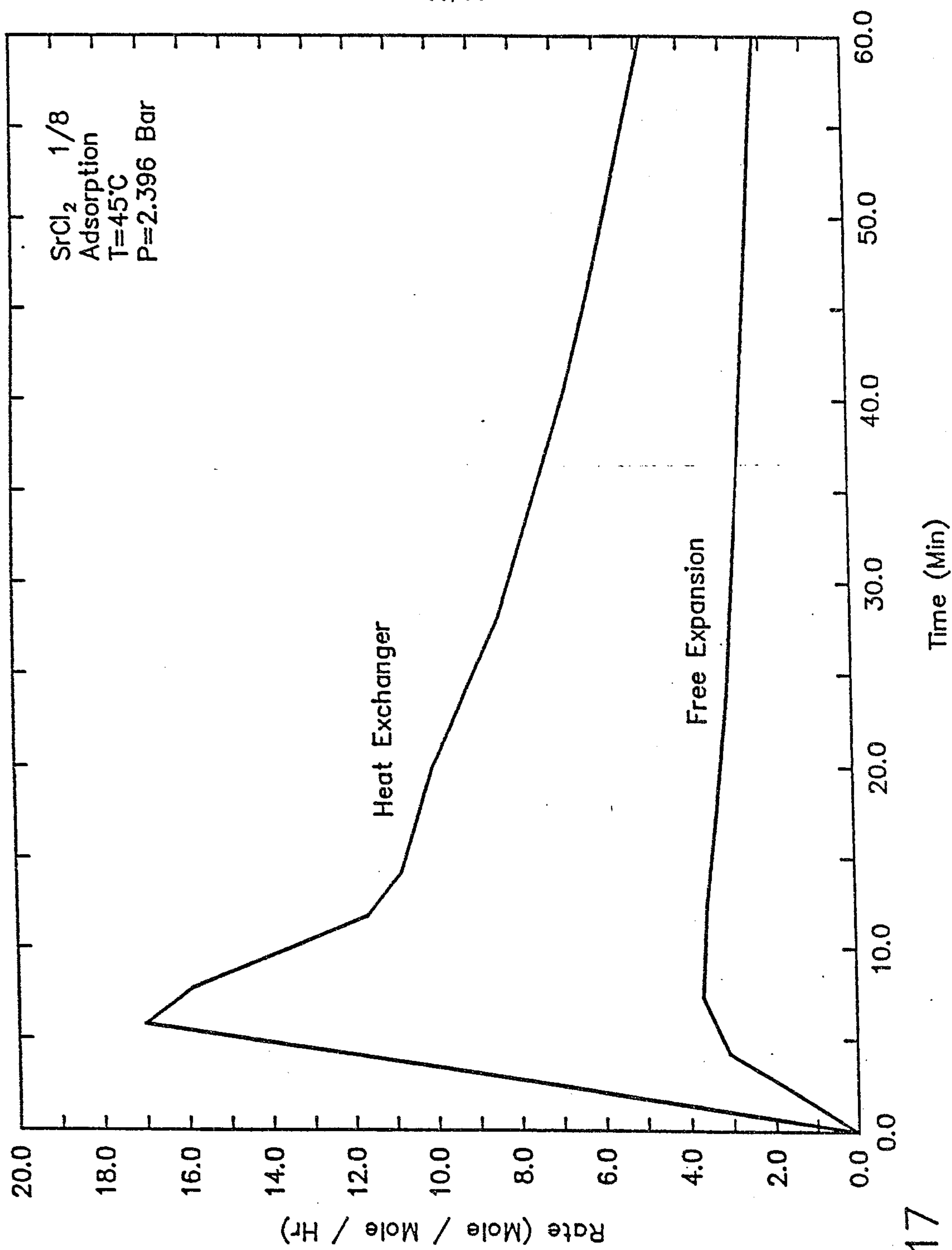


FIG. 17

