



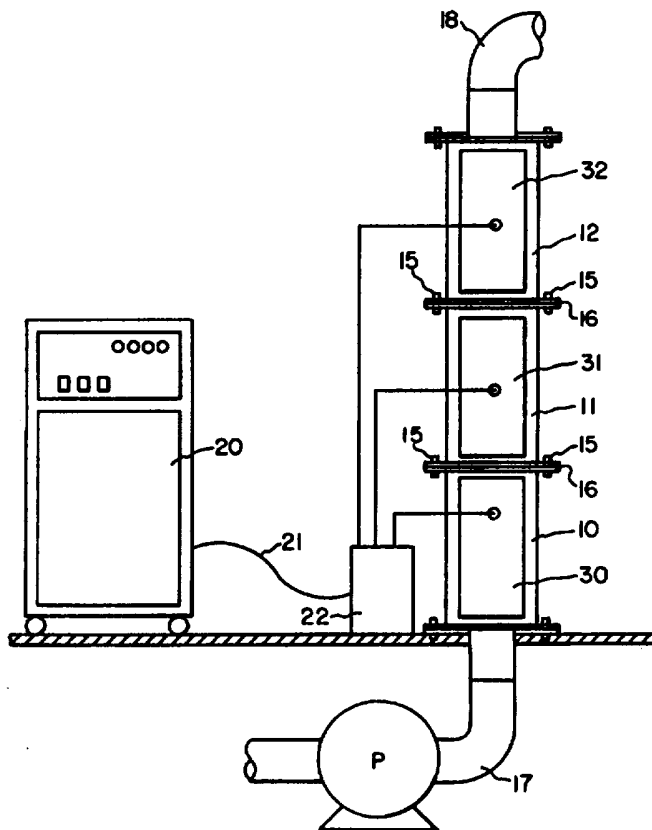
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/US96/02046 (22) International Filing Date: 14 February 1996 (14.02.96) (30) Priority Data: 08/388,744 15 February 1995 (15.02.95) US (71) Applicant: ULTRA TECHNOLOGIES INC. [US/US]; 67194 Country Club Road, Saint Clairsville, OH 43950 (US). (72) Inventor: VUJNOVIC, J., Bradley; 67194 Country Club Road, Saint Clairsville, OH 43950 (US). (74) Agents: HANSON, David, C. et al.; Webb Ziesenheim Bruening Logsdon Orkin & Hanson, 700 Koppers Building, 436 Seventh Avenue, Pittsburgh, PA 15219 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KG, KZ, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>

(54) Title: BENEFICIATION OF ORE AND COAL WITH ULTRASOUND

(57) Abstract

An apparatus for treating a slurry with ultrasound to improve separation based upon specific gravity comprises a plurality of modular conduit units (10, 11, 12) having substantially vertical walls defining a flow space through which a slurry may be pumped. Each modular conduit unit has mounted thereon ultrasound transducers (30, 31, 32) for transmitting ultrasound energy into the slurry being pumped through the modular conduit unit and means for exciting the ultrasound transducers in a frequency range of 60 to 100 kHz.



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"BENEFICIATION OF ORE AND COAL WITH ULTRASOUND"BACKGROUND OF THE INVENTION

Valuable materials are extracted from ores by
5 beneficiation processes. One beneficiation process
comprises washing wherein the valuable materials are
separated from the undesired materials on the basis of
specific gravity difference by first forming a slurry of
the crushed ore. Essential to any process of separation
10 based upon specific gravity difference is the physical
separation of the valuable materials and the undesired
materials in the slurry. This application is directed to
washing processes improved by better separation in the
slurry brought about by the efficient application of
15 ultrasound energy to the slurry. Coal washing is one
example of beneficiation by a separation based upon
specific gravity difference between the valuable and the
undesired materials.

Coal, as a fuel, is an abundant resource of
20 energy comprised mostly of carbon and small percentages of
hydrogen, sulfur and ash. When coal is burned to produce
energy, the presence of sulfur and ash is generally
undesirable. The ash enters the atmosphere as small
particles (particulates) and the sulfur as noxious sulfur
25 oxide gases. In the Appalachian coal fields, conventional
coal mining operations have traditionally refined useful
coal by washing from it less valuable sand and clay,
although fine particles of coal are often agglomerated with
the residues produced by coal washing processes. Because
30 fine coal remains a part of these residues, so-called "gob
piles" and coal slurry ponds of residues have accumulated
throughout the coal fields adjacent to coal washing yards.
These stock piles are rich in fine particles of useful
coal. In the past, it has proved to be economically
35 impractical to recover this coal.

Sulfur is present in coal in three principal
forms: pyritic sulfur (a combination of iron and sulfur),
sulfate sulfur and organic sulfur, that is, chemically
combined sulfur within the coal structure. Pyritic sulfur

can, to a large extent, be washed out of coal by conventional coal washing methods. These methods are not, however, suitably efficient on a large scale and, at best, only a small portion of the mined coal can be sufficiently
5 upgraded by washing alone. Sulfate sulfur can be separated from coal by dissolving it in water. For example, it may be boiled out of the coal matrix by elevated temperature processes which have already been developed. At the present time, there appears to be no commercial process for
10 removing substantial amounts of organic sulfur from coal.

Numerous processes have been proposed for upgrading coal to remove various forms of sulfur. The following have been considered: (1) oxidation of sulfur in the coal in an aqueous medium to form soluble sulfates; (2)
15 reduction of the sulfur to elemental sulfur in which form it can be vaporized or removed by organic solvents; (3) reaction with hydrogen to form gaseous hydrogen sulfide; (4) vapor deposition selectively on the pyritic form of sulfur followed by magnetic separation of the pyrites; (5)
20 oxidation of the sulfur with nitric oxide vapors to form gaseous sulfur oxides; (6) leaching with a sodium and calcium oxide lixiviant; and (7) leaching with aqueous ferric sulfate.

Ultrasound treatment of coal slurries has been
25 demonstrated to be useful in coal washing processes as disclosed, for example, in U.S. Patents Nos. 4,391,608 and 4,919,807. Typically, the slurry is passed through a substantially horizontal trough to which ultrasound transmitters are attached.

30 The applicant's process disclosed herein is directed to the removal of one or more of the three basic forms of sulfur from coal and coal-like materials. At the same time, the process reduces the amount of ash within the coal or coal-like material. The recovery of useful coal is
35 improved and the ability of the coal product to shed water is increased. The process involves the use of atmospheric pressures and low temperatures (temperature near room

temperature) and may be practiced with rugged processing equipment. Further, the process improves the characteristics of the residue thereby enhancing their disposition and reducing problems with their disposal and
5 allowing potential beneficial uses of them.

It should be understood that the processes and apparatus disclosed herein have application not only to coal washing but also to the beneficiation of mineral ores, for example, gold ore and tailings from gold ore
10 beneficiation, wherein the valuable materials and gangue (unwanted materials) can be separated on the basis of specific gravity difference. Indeed, in some ways these processes and apparatus have greater application to separation of heavier and more abrasive materials than raw
15 coal. An additional advantage of this invention is the minimization of the abrasive action of the slurry on the apparatus for applying ultrasound to the slurry.

The inventor does not wish to be limited by any particular theory of operation but it is understood that
20 sound waves in liquids comprise expansion cycles and compression cycles. During the expansion cycle, the molecules of the liquid are separated creating a gap or "cavity" in the liquid. The cavity only exists until the next compression cycle at which time the cavity rapidly
25 implodes. This implosion creates a microscopic jet directed at or along the surface of solids within the liquid and also rapidly heats the liquid surrounding the cavity (which is almost instantaneously cooled by the large mass of liquid). The combination of extremely hot liquid
30 and microscopic jets work upon the surfaces of the solids.

In the past, ultrasound energy having frequencies in the range of about 10 to 50 kHz have been suggested for treatment of coal slurries. This was based in part upon the expected attenuation of sound energy as it progresses
35 into the slurry. The higher the frequency, the more rapid the attenuation. According to the invention disclosed herein, much higher frequencies are contemplated. The

doubling of frequency doubles the number of locations within the slurry about which cavitation and implosion take place, thus increasing the action of the ultrasound on smaller and smaller particles because the implosion
5 locations are closer to one another.

SUMMARY OF THE INVENTION

Briefly, according to this invention, there is provided a method and apparatus for treating an ore slurry with ultrasound to improve separation based upon specific
10 gravity. The invention comprises passing the ore slurry vertically through a conduit and applying ultrasound energy to the slurry passing through the conduit having frequencies in the range of 60 to 100 kHz, preferably 70 to 90 kHz.

15 A specific embodiment of this invention comprises a method for treating coal to reduce the ash and sulfur content and for improving the characteristics of a resulting residue. The method comprises a first step for combining the coal with water to form a slurry, a second
20 step for applying ultrasound of a frequency between 60 and 100 kHz, preferably about 80 kHz, to said slurry which breaks the physical bonds of ash and sulfur from the coal and a third step for physically separating the ash and sulfur from the coal to recover coal with reduced sulfur
25 and ash content by using such devices as cyclone separators, spiral separators, vibrating screens or centrifuge separators. Preferably, the coal is first crushed and sized to pass a one-quarter inch mesh screen. It is preferred that the temperature of the slurry is
30 maintained less than 75° C. According to a preferred method, the weight ratio of coal to water in the slurry comprises between 1:20 and 1:3.

There is also provided, according to this invention, an apparatus for treating a slurry prior to
35 separation based upon specific gravity, for example, to separate coal from contaminants containing ash and sulfur. The apparatus comprises a plurality of modular conduit

units having substantially vertical walls defining a flow space through which the slurry may be pumped. Each conduit unit has mounted thereon ultrasound transducers for transmitting ultrasound energy into the slurry being pumped
5 through the conduit unit. An electrical power supply is provided for exciting the ultrasound transducer units in a frequency range of 60 to 100 kHz, preferably 70 to 90 kHz. Preferably, the conduit units have a section perpendicular to the direction of flow of slurry such that no volume of
10 the slurry passes through the conduit more than about three inches from a transducer and preferably two inches from the transducer. Preferably, the modular units are arranged with flanges at the top and bottom that enable connecting them to adjacent modular units or inlet and outlet conduits
15 for carrying slurry to and from the apparatus. In an especially preferred embodiment, each conduit unit has a rectangular cross section with transducers mounted on at least two opposing walls. Preferably, according to this invention, there is provided a pump for pumping slurry
20 through the conduit at a rate of about 2 feet per second (1.2 meters/second). In an especially preferred embodiment of this invention, a pump is connected to the modular conduit unit such that slurry is pumped up through the conduit units.

25 BRIEF DESCRIPTION OF THE DRAWINGS

Further features and other objects and advantages will become apparent from the following detailed description made with reference to the drawings in which:

30 Fig. 1 is a schematic view of a unit for treating a slurry with ultrasound according to this invention comprising three modular conduit units with internally mounted transducer units;

Fig. 2 is a top view of one modular unit shown in Fig. 1;

35 Fig. 3 is a side view in section of one modular unit shown in Fig. 2; and

Figs. 4 and 5 are front and side views, respectively, of a modular conduit unit for treating a slurry with ultrasound comprising five modular conduit units with externally mounted transducer units.

5 DESCRIPTION OF THE PREFERRED EMBODIMENTS

The techniques of this invention provide effective and economic methods for beneficiating crushed or granulated coal fines by reducing the sulfur and ash (e.g., sand and coal) content. In the case of coal gob piles and
10 coal slurry ponds, it achieves efficient recovery of valuable coal while also improving the characteristics of the remaining residue for densely packed backfilling of coal mining pits, open or underground, and filling the voids of the underground excavations to prevent subsidence
15 and reducing the settling times for ponds and settling basins to produce clarified wash water for recycling or other uses.

The first step of this method requires crushing and preferably sizing the coal to a more or less uniform
20 size. A particular size to be selected depends upon the type of coal and the amount of sulfur that must be removed and, of course, the type of sulfur within the coal itself. Certain coals have been found to respond to treatment very well if crushed to pass a one-quarter inch mesh screen. It
25 should be understood that the process described herein can be used for the treatment of residue from coal washing processes sometimes referred to as pond coal, in which case the starting material is already very fine, say minus 28 mesh Tyler. In this instance, it is not necessary to crush
30 and size the coal starting material. The second step comprises combining the coal with water in a bath to form a slurry. A third step involves applying ultrasound to the slurry. This is done by continuously pumping the slurry through an ultrasound cell where it is resident for only a
35 relatively short period of time. A fourth step comprises physical separation to recover a coal with a reduced sulfur and ash content and then removing the coal from the water.

In using ultrasonics in connection with liquids, normally, cavitation will occur in liquids and is produced by transducer acceleration pressures against the liquid slurry. Cavitation is the formation of partial vacuums
5 within the liquid. Ultrasonically induced cavitation appears to promote chemical as well as physical changes of substances within the liquid to which the sound is applied. An important aspect of this invention is the provision of a unique unit for applying ultrasound to a coal slurry
10 wherein the coal slurry is passed through the ultrasound unit in a substantially vertical direction and ultrasound waves having a frequency on the order of 80 kHz (60-100 kHz) are transmitted into the slurry by transducers mounted on the substantially vertical walls of the unit. For
15 ultrasonic treatment, when water is used as a treatment medium, cavitation and agitation may both be involved. Temperature affects the speeds and frequency of ultrasonic waves within a given medium. Generally, at about a
20 temperature of 73° C, cavitation and frequency of ultrasonic waves within water begin to deteriorate. It is, therefore, desirable to keep the slurry below 73° C.

The ultrasonic waves created in the slurry as it passes through the ultrasound unit result in breaking the physical bonds of the fine coal particles from the
25 particles of ash or sulfur compounds. After the physical bonds are severed by this ultrasonic treatment, physical separation using a cyclone has been found to be highly effective and the coal particles are also found to be cleaned by the ultrasonic treatment. This also increases
30 the number of BTUs recoverable per pound. The amounts of retained water in the recovered constituent are also decreased as compared to other recovery systems and fine pyritic and organic sulfur constituents are decreased.

The "gob piles" remaining after conventional coal
35 washing operations may contain from 25% to 50% coal particles. After this refuse material is optionally crushed and screened to pass a one-quarter inch mesh

screen, it is ready for treatment in the apparatus of the present invention, permitting recovery of as much as 70% or more of the coal in the gob pile and slurry ponds.

The same technique can be used to separate gold
5 and other valuable minerals from crushed ore. The ultrasonic energy breaks the surface tension bonds between mineral particles and ash/clay particles and any air bubbles, gels, slime or algae causing particles to adhere together. This process may be called microscopic scrubbing
10 of the particles and it produces unusually clean particle surfaces, stripped of foreign material and carrying much less moisture than before.

Self-compaction of these ultrasonic scrubbed fine particles, unimpeded by air bubbles, gel particles or other
15 foreign coatings, leads to denser filter cakes or sludge layers. It will be understood that the rates of screening, filtration, conveying, heat transfer and drying of the resulting scrubbed fine particles are all enhanced by these processes of the invention and the effective recovery of
20 mineral particles from crushed ore slurries are significantly improved.

Finally, subsequent operations such as centrifugal separation steps are made more efficient when they are performed on the slurries treated in the
25 ultrasound unit of this invention.

Once the mineral constituents are treated as in the present invention, the minerals and residue follow more closely Stokes law in settling in calm water. Stagnant ponds of gangue, tailings, coal and other materials often
30 contain gelatinous material which encase the small solid particles. Ultrasound disintegrates and separates the water-gel layer and also algae from these small solid particles. The microscopic scrubbing action is believed to account for many of the advantages of the ultrasonic
35 cleaning process. For example, with the surface tension removed, the dewatering rate and the sedimentation or settling rate for resulting fine particles are notably

improved after the ultrasonic treatment of these slurries. This leads to rapid clarification of settling basins and pond water because of this enhanced clean separation of mineral particles from each other and from gel, algae and
5 the like. The rapid settling of the fines enables larger amounts of coal to be washed by a coal processing plant because the clarifier can process the waste material much more efficiently. The rate of screening these clean fine particles is also improved following this ultrasonic
10 treatment of slurries and clogging buildups of fines on screens is greatly reduced when the fine particle surfaces are cleaned in this manner. In all cases, the clarification of the pond water is greatly improved and in some cases the settling rates for the fines are increased
15 as much as ten times. Chemical additives such as flocculating agents are made significantly more efficient by these processes. For example, when they are used with the processes of this invention, the normal amounts of flocculants may be reduced by as much as 80% to 95% without
20 adversely affecting the operating results.

Apparatus

Referring now to Fig. 1, there is shown a schematic view of a unit for treating a slurry with ultrasound. The unit comprises a column of three modular
25 conduit units 10, 11 and 12 having flanges on each end enabling them to be joined together by fasteners 15 which clamp rubber gaskets 16 between the flanges to seal the modular units together. The modular design has a beneficial benefit in that the length of the column
30 comprised of modular units can be extended when necessary to increase the amount of ultrasound energy applied to the slurry. A column of modular units is connected at one end to an intake conduit 17 which is in communication with a pump P that draws slurry to be processed from a sump or the
35 like. The column is connected at the upper end to an outflow conduit 18 which connects the ultrasonically treated slurry to the cyclone separators (not shown) or the

like. A power supply 20, a cable 21 which may extend up to 30 feet, and a quick disconnect box 22 supply electrical energy to the ultrasound transducers 30, 31 and 32 mounted in each modular conduit unit. The modularity of the 5 conduit units and the quick disconnect box enable the rapid replacement of modular units when maintenance is required minimizing the down time of the coal washing plant.

Referring now to Fig. 2, there is shown top and bottom sections of modular units having immersible 10 ultrasound transducers mounted therein. The transducer units are hermetically sealed containers having a plurality of piezoelectric crystals mounted therein. According to a preferred embodiment, each immersible transducer unit is capable of outputting 7,200 watts peak output power.

Referring now to Figs. 4 and 5, there is shown in front and side view a column comprised of modular conduit units 40, 41, 42, 43 and 44 having the ultrasound transducers 46 mounted on the exterior thereof.

Comparative Testing

20 Example I

Gob pile coal was processed according to this invention. The raw coal had the following analysis after drying:

	ash:	43.90 wt. %
25	volatile matter:	14.05 wt. %
	fixed carbon:	42.05 wt. %
	Total:	100%
	sulfur:	2.18 wt. %
30	heat content (BTU/pound):	8,175 (4542 kcal/kg)

This coal is far from complying with environmental regulations in the United States. To be a compliance coal, a coal must have less than 0.72 weight percent sulfur at a heat content of 12,000 BTU per pound.

35 This coal in slurry form was processed as follows and separated in a cyclone separator.

length of ultrasound column: 66 inches (168 cm)
width of column: 4 inches (10 cm)
frequency of ultrasound: 80 kHz
total power: 7,200 x 3 watts
5 flow rate of slurry: 2 feet per second
(1.2 meters/second)
direction of flow: upward

Two samples were dried after separation and were analyzed as follows:

10		<u>Sample 1</u>	<u>Sample 2</u>
	ash:	13.41 wt. %	12.51 wt. %
	sulfur:	0.86 wt. %	0.88 wt. %
	heat content (BTU/pound):	13,457	13,630
15		(6852 kcal/kg)	(7574 kcal/kg)

With adjustment of the cyclone separator, it would be expected that the ash could be further reduced as with the following example. This product with typical moisture would be near compliance and with the ash further
20 reduced it would be brought into compliance.

Example II

In yet another test, the coal taken from a pond was analyzed as follows:

		<u>Sample 3</u>	<u>Sample 4</u>
25	ash:	45.27 wt. %	52.8 wt. %
	sulfur:	3.38 wt. %	3.46 wt. %

Materials from which Samples 3 and 4 were taken were combined, crushed to all pass 1/4 inch (.64 cm), and passed through the apparatus as described above in Example
30 I with and without the ultrasound turned on. The slurry was separated in the laboratory on the basis of a specific gravity of 1.45. The results were as follows:

		<u>80 kHz ultrasound on</u>	<u>no ultrasound</u>
	ash:	8.6 wt. %	11.08 wt. %
35	sulfur:	0.77 wt. %	1.15 wt. %
	recovery:	38.7 wt. %	27.47 wt. %
	heat content (BTU/pound):	14,258	13,676
		(7911 kcal/kg)	(7599 kcal/kg)

Examples I and II establish the substantial benefit of processing slurries according to the teachings of this invention. Referring to Example II, not only is the product lower in ash and sulfur content resulting in a compliance coal product but the amount of clean coal recovered is increased by 40%. This, in itself, is a substantial advantage of applicant's method.

Having thus described my invention with the detail and particularity required by the Patent Laws, what is claimed to be protected by Letters Patent is set forth in the following claims.

I CLAIM:

1. An apparatus for treating a slurry with ultrasound to improve separation based upon specific gravity comprising:

5 a plurality of modular conduit units having substantially vertical walls defining a flow space through which a slurry may be pumped;

10 each said modular conduit unit having mounted thereon ultrasound transducers for transmitting ultrasound energy into the slurry being pumped through said modular conduit unit; and

means for exciting the ultrasound transducers in a frequency range of 60 to 100 kHz.

2. An apparatus according to claim 1, wherein the conduit has a section perpendicular to the direction of flow such that no volume of slurry passing through the conduit passes more than about three inches from a
5 transducer.

3. An apparatus according to claim 1, wherein each modular unit has attachment flanges at top and bottom that enable connection to adjacent modular units or inlet and outlet conduits for carrying slurry to and from the
5 apparatus.

4. An apparatus according to claim 1, wherein each conduit unit has a rectangular cross section with transducers mounted on at least two opposing walls.

5. An apparatus according to claim 1, further comprising a pump for pumping slurry through the conduit at a rate of about 2 feet per second.

6. An apparatus according to claim 5, wherein the pump and apparatus are connected to pass the slurry up through the conduit.

7. An apparatus according to claim 1, wherein the length of the modular units in the flow direction is about 20 inches.

8. An apparatus according to claim 1, wherein the transducers in the modular units and the means for exciting the transducers input at least 7,200 watts per modular unit.

9. A method of treating coal to reduce ash and sulfur content and improving the characteristics of resulting residue comprising the steps for:

- 5 (a) combining the coal with water to form a slurry;
- (b) passing the slurry through a conduit in the vertical direction such that no volume of the slurry passes more than three inches (7.5 cm) from an ultrasound transducer;
- 10 (c) applying ultrasound of a frequency between 60 and 100 kHz to said slurry to cause separation of ash and sulfur from coal; and
- (d) physically separating coal from the slurry to separate ash and sulfur from the coal to recover coal
15 with reduced sulfur and ash content.

10. A method of treating mineral ores such as tailings from gold ore beneficiation which ores comprise a valuable mineral fraction and a worthless gangue fraction comprising the steps for:

- 5 (a) combining the ores with water to form a slurry;
- (b) passing the slurry through a conduit in a vertical direction such that no volume of the slurry passes

more than three inches (7.5 cm) from an ultrasound
10 transducer;

(c) applying ultrasound of a frequency between
60 and 100 kHz to said slurry; and

(d) physically separating the valuable mineral
fraction from the gangue fraction.

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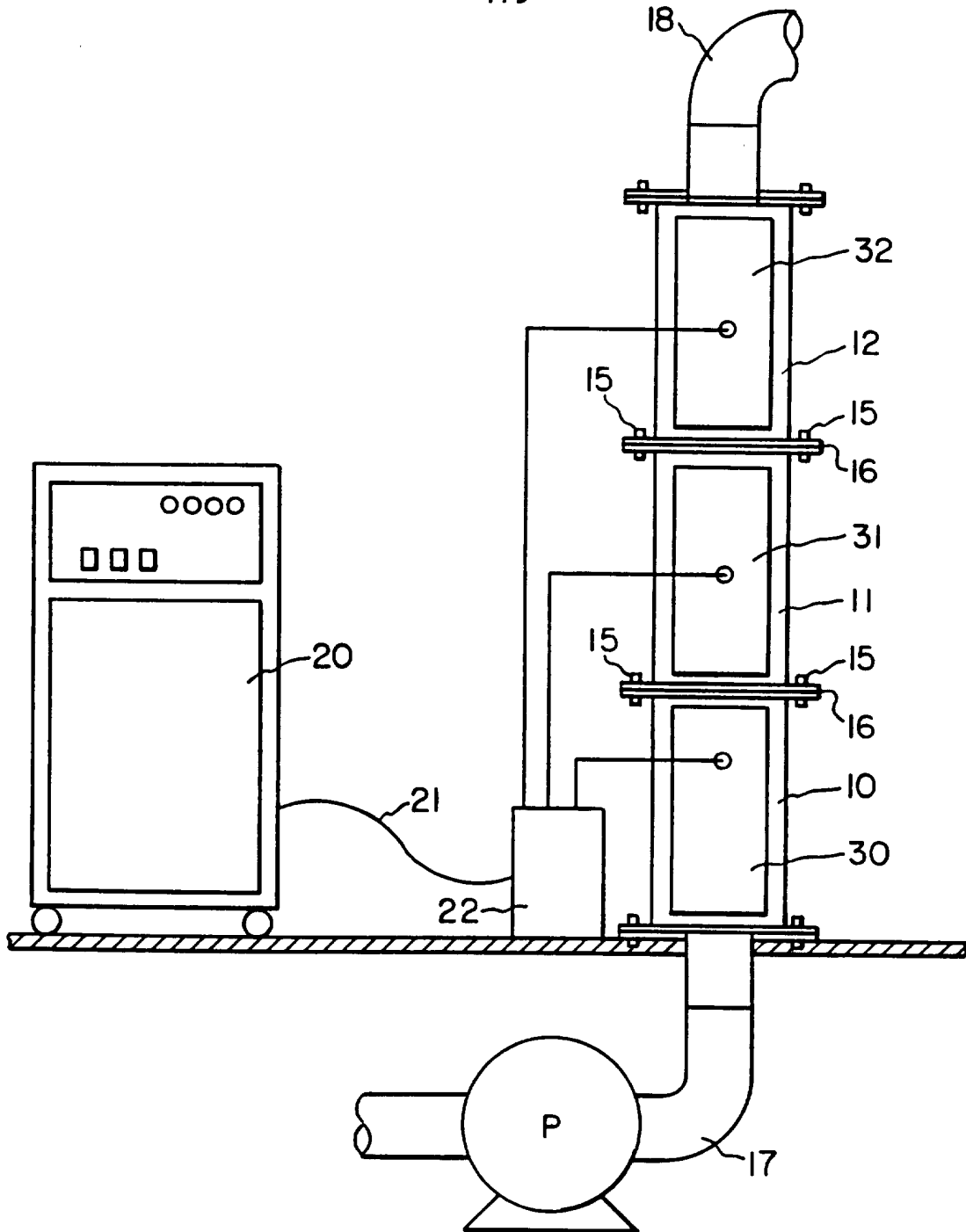


FIG. 1

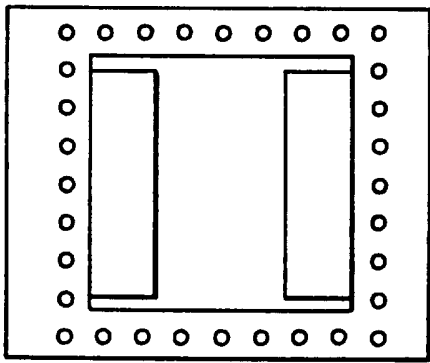


FIG. 2

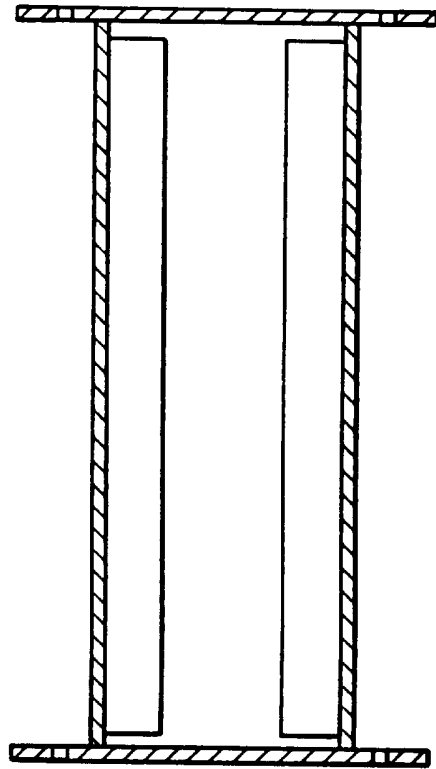


FIG. 3

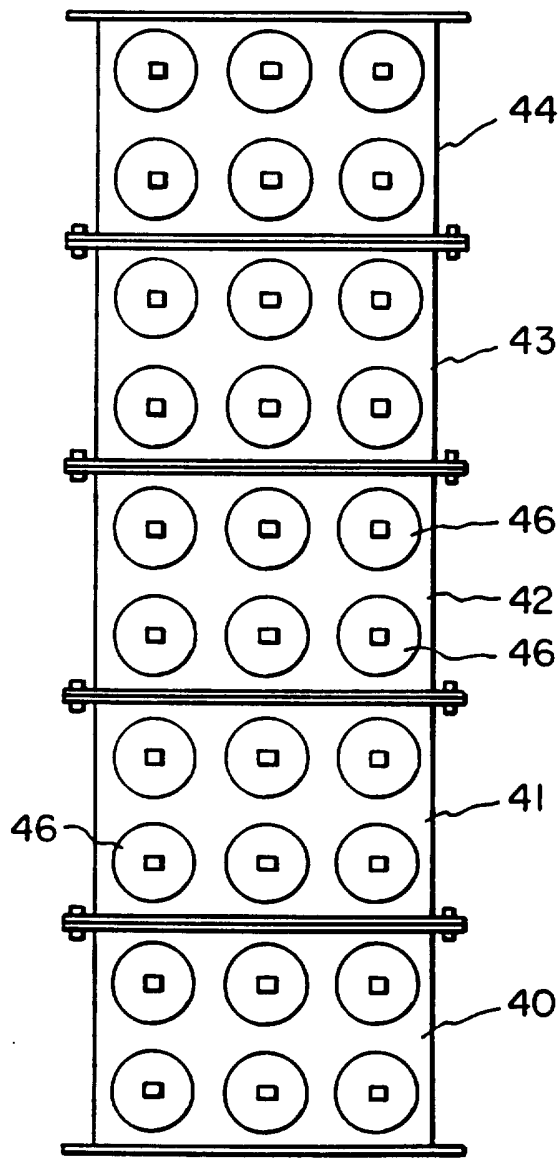


FIG. 4

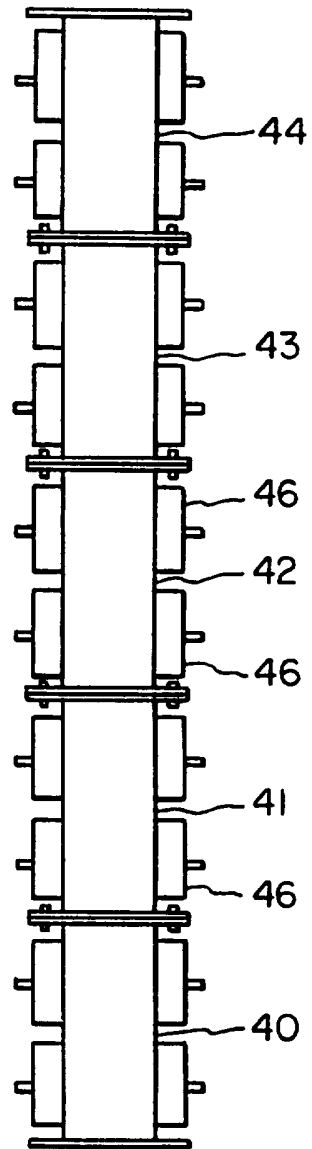


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/02046

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B02C 19/18
US CL :241/1, 301

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/280, 281, 282, 904
241/1, 21, 301, 20, 24, 29, 285.2

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,556,467 (KUHN ET AL.) 03 DECEMBER 1985, SEE ENTIRE DOCUMENT.	1-10
Y	US, A, 3,545,683 (SCHULTE) 08 DECEMBER 1970, SEE ENTIRE DOCUMENT.	1-9
Y	US, A, 3,207,447 (WHITHAM) 21 SEPTEMBER 1965, SEE ENTIRE DOCUMENT.	1-9
Y	DD, A, 246,706 (RAATZ ET AL.) 17 JUNE 1987, SEE ENTIRE DOCUMENT.	1-9
Y	US, A, 4,537,599 (GREENWALD) 27 AUGUST 1985, SEE ENTIRE DOCUMENT.	10

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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23 APRIL 1996

Date of mailing of the international search report
16 MAY 1996

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