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(54) Heat exchange process and heat exchanger

(57) Heat exchange process comprising sequential cooling a first fluid by indirect heat exchange with a second fluid and comprising the following steps:

- introducing the first fluid sequentially into at least two concentric U-tube bundles defining at least a first heating zone and a second heating zone respectively,
- introducing a second fluid onto the shell side of the U-tube bundles, each heating zone partially separated from the other by a wall, the first heating zone being a colder zone and the second heating zone being a hotter zone, the tube bundle of the first colder heating zone being made of a low alloy steel and the tube bundle of the second hotter heating zone being made of a temperature and corrosion resistant alloy,
- withdrawing the cooled second fluid and the heated first fluid.

The invention also concerns a heat exchanger for use in the above process.

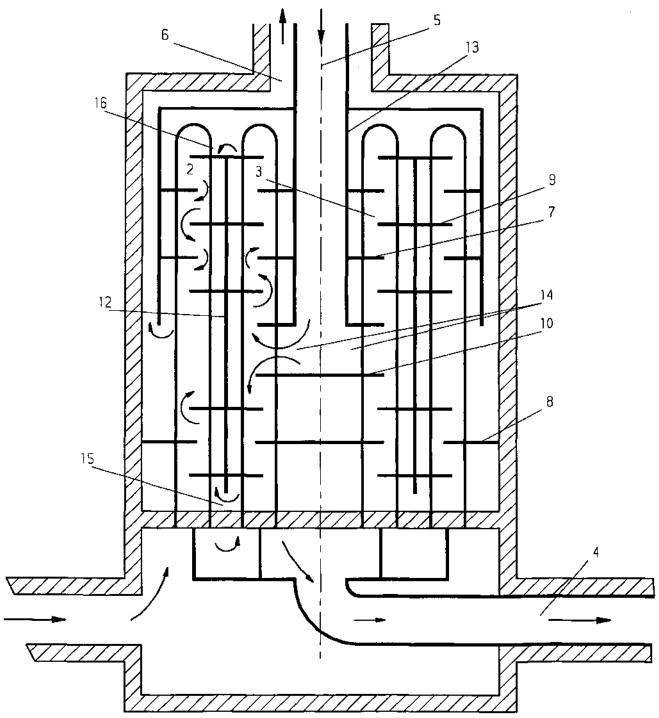

FIG. 1

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Description

[0001] The invention concerns a heat exchanger and a process for heat exchange in which the heat exchanger is applicable. In particular the invention relates to a heat exchanger useful as a steam super heater and having improved resistance to metal dusting and stress corrosion.

BACKGROUND OF THE INVENTION

[0002] Steam reforming is most often an essential step in the production of carbon monoxide rich synthesis gas. In this reaction methane and steam is hereby converted under supply of heat to a gas composition comprising hydrogen, carbon dioxide, carbon monoxide, steam and methane. The temperature of the synthesis gas after reforming is most often between 750°C and 1050°C. The hot synthesis gas is subsequently cooled in a boiler or in a boiler and a super heater.

[0003] One of the severe conditions related to coolers for reformed gas is the corrosion known as metal dusting. Metal dusting is a deteriorating attack of the carbon monoxide rich gas on alloys based on iron and/or nickel. A basic reaction by metal dusting is the decomposition of carbon monoxide in a reduction reaction or the bouduard-reaction. Metal dusting only takes place when the metal surface temperature is below the equilibrium temperature of these reactions. That will typically be between 750°C and 850°C. However, if the temperature is lower, typically below 450°C, the reaction will not take place at a significant rate. This means that there is a metal temperature surface intermediate, which should be avoided for contact with gas in reformed gas coolers. These temperature ranges are between 450-800°C for nickel based high alloys and 400-800°C for low alloy steels.

[0004] The heat transfer surfaces of waste heat boilers are cooled by the effective heat transfer to the boiling water and can therefore normally be designed to avoid conditions of metal dusting. However, super heaters when applied as coolers for synthesis gasses have to be considered as subject to metal dusting attack.

[0005] Another severe condition to consider in the design of super heaters is the possibility of stress corrosion from the wet steam which is to be superheated. Nickel based alloys are very sensitive to stress corrosion, whereas low alloy steels are not. Nickel based alloys should therefore only be in contact with dry steam.

[0006] It is therefore an objective of the invention to provide a heat exchanger which shows improved resistance to metal dusting and stress corrosion.

BRIEF SUMMARY OF THE INVENTION

[0007] The invention provides a heat exchange process comprising sequentially cooling of a first fluid by indirect heat exchange with a second fluid and comprising the following steps:

- introducing the first fluid sequentially into at least two concentric U-tube bundles defining at least a first heating zone and a second heating zone respectively,
- introducing a second fluid onto the shell side of the U-tube bundles, each heating zone partially separated from the other by a wall, the first heating zone being a colder zone and the second heating zone being a hotter zone, the tube bundle of the first colder heating zone being made of a low alloy steel and the tube bundle of the second hotter heating zone being made of a temperature and corrosion resistant alloy,
- withdrawing the cooled second fluid and the heated first fluid.

[0008] The invention also provides a heat exchanger for use in the above process, the heat exchanger for use in the above heat exchange process, the heat exchanger comprising a plurality of U-tubes securing a heat exchange surface for allowing heat transfer between a first and a second fluid, the U-tubes arranged in at least two sequential concentric tube bundles, the tube bundles defining at least a first and second heating zone respectively, each heating zone partially separated from the other by a wall, the first heating zone being a colder zone and the second heating zone being a hotter zone, the tube bundle of the first colder heating zone being made of a low alloy steel and the tube bundle of the second hotter heating zone being made of a temperature and corrosion resistant alloy.

BRIEF DESCRIPTION OF THE FIGURES

[0009]

Figure 1 shows a heat exchanger with two heating zones.

Figure 2 shows a horizontal section through a heat exchanger.

Figure 3 shows a heat exchanger with three heating zones.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The invention concerns a heat exchanger which is useful as a super heater and is designed to avoid metal dusting and stress corrosion by a proper selection of a combination of metal alloys and gas/steam flow through a pre-defined pattern of heat exchange tube bundles. The heat exchanger is suitable for heat exchange between a first and a second fluid. An example of such fluids is steam (first fluid) and synthesis gas (second fluid). The hot synthesis gas from a steam reforming reactor is cooled by steam in the heat exchanger.

[0011] The heat exchanger is of the U-tube type with a thick tube sheet. A plurality of U-tubes for transfer of the first fluid are arranged parallel and spaced apart with a central inlet and a peripheral outlet for the second fluid. The shell side heat exchange is enhanced by disc and doughnut baffles. The plurality of tubes is arranged in tube bundles, each tube bundle corresponding to a particular heating zone.

[0012] The first fluid, for instance steam, flows in the tubes and the second fluid, for instance reformed gas, flows around these tubes, i.e. on their shell side, thereby securing a heat transfer surface.

[0013] The essential principle of the invention is that at least two tube bundles are present in the heat exchanger and they are connected to one tube sheet in concentric rings. The compartments for each tube bundle are separated by metallic walls with openings in their middle or at their ends through which the second fluid passes and is divided into several streams when flowing from one compartment to the other.

[0014] The second fluid flows both countercurrent- and concurrent to the first fluid within each tube bundle compartment, as shown by the arrows in figures 1 and 3.

[0015] The heat exchanger of the invention will be described in more detail in the following:

In figures 1 and 3 the flow directions of the first and second fluids are indicated by curved arrows.

[0016] Figure 1 relates to an embodiment of the invention having two heating zones separated by a wall. The first fluid, for instance steam, enters the heat exchanger through inlet 1. The first fluid then enters a compartment comprising U-tubes in a first tube bundle and defining a first heating zone 2. After passing through the U-tubes in the first heating zone in indirect heat exchange with the second fluid, the first fluid enters a second compartment comprising the U-tubes in a second tube bundle and defining a second heating zone 3.

[0017] The U-tubes of the second tube bundle are placed sequentially after the U-tubes of the first tube bundle. In figure 1 the tube bundle defining the second heating zone 3 is placed innermost in the heat exchanger while the tube bundle defining the first heating zone 2 is placed outermost and the two tube bundles are separated by a wall 12. The wall 12 can be of metal and it is positioned and constructed to provide openings 15 and 16 allowing division of the flow of the second fluid into several streams, when flowing from one compartment to the other. The first fluid passes through the U-tubes in the second heating zone 3 in indirect heat exchange with the second fluid. After passing through the second heating zone 3 the first fluid is now heated and it leaves the heat exchanger through the outlet 4.

[0018] The second fluid, for instance synthesis gas, or any other hot gas that requires cooling, enters the heat exchanger through inlet 5. Inlet 5 leads to a central pipe 13 placed in the middle of the innermost tube bundle. This central pipe 13 has openings 14 allowing the second fluid to leave the central pipe 13 and enter the second heating zone 3 on the shell side of the tube bundles defining this heating zone. It is preferable that the openings 14 are not located at the ends of the central pipe 13, in order to ensure both concurrent and countercurrent flow.

[0019] The second fluid enters the middle of heating zone 3 through the openings 14 and the fluid is then divided to flow towards the two ends of the tube bundle. The second fluid thus contacts the external surfaces i.e. the shell side of the U-tubes of the innermost tube bundle and is cooled in indirect heat exchange with the first fluid. The second fluid thereafter passes through end openings 15 and 16 in the wall 12 separating the two tube bundles defining the first and second heating zones 2 and 3. The opening 15 is at the lower end of the wall 12 and the opening 16 is at the upper end of the wall 12. The second fluid then passes across the shell side of the tube bundles defining the first heating zone 2, which surrounds the innermost bundle defining the second heating zone 3. The gas then flows in the tube bundle from the end openings 15 and 16 towards the middle of the heating zone 2. The further cooled second fluid then leaves the first heating zone 2 and the heat exchanger through outlet 6.

[0020] Figure 2 shows the placement of the tube bundles relative to each other in the heat exchanger. The wall 12 divides the heating zones into two compartments resulting in heating zones 2 and 3. The tube bundles are placed in the heat exchanger with the tube bundle of heating zone 2 placed outermost and the tube bundles of heating zone 3 placed innermost.

[0021] In an embodiment of the invention, the heat exchanger can have three heating zones, as shown in figure 3. In this case there is a third bundle of U-tubes surrounding the second bundle. The third bundle also defines a heating zone 11 allowing further heat exchange of the first fluid with the second. The second fluid enters the middle of this heating zone through a central opening 17 in the wall 18 separating the outermost tube bundle from the two innermost tube bundles. The wall 18 separates thereby heating zone 11 from heating zones 2 and 3. The fluid is then divided into streams flowing towards the two ends of the tube bundle.

[0022] The walls separating the compartments can therefore have openings at either their ends (15 and 16) or in their middle (17). When several heating zones are at present the openings in each subsequent wall therefore alternate by being either at the end of the wall or in its middle. This ensures that the flow of the second fluid is both concurrent and counter current to the flow of the first fluid in each heating zone. Effective heat exchange is thereby realised.

[0023] The second fluid is in this way cooled by subsequent flow (divided flow) through the two or three tube bundles. When two heating zones are present as shown in figure 1, the first fluid is heated by subsequent flow through the tubes, starting in the outermost bundle, which is coldest and has the lowest temperature and leaving after flow through the innermost bundle, which is hottest and therefore has the highest temperature. The outmost tube bundle defining the heating zone 2 therefore corresponds to a cold zone (a low temperature zone) and the innermost bundle defining the heating zone 3 therefore corresponds to a hot zone (a high temperature zone).

[0024] When three heating zones are present as shown in figure 3, the heating zone 2 in the middle between heating zones 3 and 11, has intermediate temperatures between the hottest (high temperature zone) and the coldest (low temperature zone) zones.

[0025] Baffles can be placed in the heating zones in order to improve the heat distribution. Baffles particularly suitable for the heat exchanger are of the disc and doughnut type. These have the effect of allowing the second fluid to travel through the heating zones in a zigzag movement and additionally they assist in positioning the U-tubes. The baffles 7, 8 and 9 shown in figure 1 are held in place by rods. Baffle 7 is hot i.e. experiences high temperature, and baffle 8 is cold i.e. experiences low temperature. The baffles 10 in the central pipe are hot baffles. Baffles can also be placed in the embodiment shown in figure 3.

[0026] The hot (high temperature) tube bundle defining heating zone 3 must be made of a material resistant to metal dusting. This could for example be a high alloy such as austenitic nickel/chromium/iron alloy, for instance Inconel®. The baffles, rods and walls defining the channels in which the tube bundles are situated must also be resistant to metal dusting. The cold (low temperature) tube bundle defining heating zone 2 may be of low alloy steel and in most cases the baffles and rods may also be of low alloy material. If a third bundle of tubes are present as shown in figure 3, the tubes of the middle/intermediate bundle may be of low alloy steel, whereas the rods, baffles and walls/channels may be of Inconel®. The low alloy steel could for example be a ferritic iron, chromium, molybdenum, carbon steel.

[0027] Characteristic for the heat exchanger of the invention is that the U-tubes are of materials resistant to metal dusting when the material surface is hot enough to give a risk of metal dusting. The U-tubes can be of cheaper low alloy steel when situated in colder zones. Low alloy steel is not sensitive to wet stress corrosion. When the first fluid is steam, it enters U-tubes of low alloy steel, and the steam will not come in contact with the U-tubes of high alloys before it is completely dry.

[0028] The heat exchanger of the invention shows an improvement in its heat exchange performance due to it enhanced resistance towards metal dusting and stress corrosion.

[0029] A typical process in which the heat exchanger is useful is in a steam reforming process as described in the following:

Hot effluent, for instance a carbon monoxide containing reformed gas such as synthesis gas from a reforming reactor, is passed to a waste heat boiler where the temperature of the effluent is reduced from, for instance 1050°C to 475°C, using steam supplied from a steam drum. The cooled effluent is then sent to a heat exchanger of the invention where the temperature is further reduced to 360°C by heat exchange with steam. The heat exchanger functions as a steam super heater. The steam used can be supplied from the steam drum and it is thereby heated from a temperature of for instance 320°C to 400°C.

Claims

1. Heat exchange process comprising sequentially cooling a first fluid by indirect heat exchange with a second fluid and comprising the following steps:

   - introducing the first fluid sequentially into at least two concentric U-tube bundles defining at least a first heating zone and a second heating zone respectively,
   - introducing a second fluid onto the shell side of the U-tube bundles, each heating zone partially separated from the other by a wall, the first heating zone being a colder zone and the second heating zone being a hotter zone, the tube bundle of the first colder heating zone being made of a low alloy steel and the tube bundle of the second hotter heating zone being made of a temperature and corrosion resistant alloy,
   - withdrawing the cooled second fluid and the heated first fluid.

2. Heat exchange process according to claim 1, wherein the first fluid is steam and the second fluid is reformed gas.

3. Heat exchange process according to claim 1, wherein the temperature and corrosion resistant alloy is austenitic nickel/chromium/iron alloy.

4. Heat exchange process according to claim 2, wherein the heated first fluid is superheated steam.

5. Heat exchanger for use in the process of claim 1, comprising a plurality of U-tubes securing a heat exchange surface for allowing heat transfer between a first and a second fluid, the U-tubes arranged in at least two sequential concentric tube bundles, the tube bundles defining at least a first and second heating zone respectively, each heating zone partially separated from the other by a wall, the first heating zone being a colder zone and the second heating zone being a hotter zone, the tube bundle

of the first colder heating zone being made of a low alloy steel and the tube bundle of the second hotter heating zone being made of a temperature and corrosion resistant alloy.

6. Heat exchanger according to claim 5, wherein the heat exchanger has three tube bundles, the third bundle being placed in the middle between the first and the second bundles.

7. Heat exchanger according to claim 5, wherein the temperature and corrosion resistant alloy is austenitic nickel/chromium/iron alloy.

8. Heat exchanger according to claim 5, wherein the heat exchanger has baffles of the disc and doughnut type.

9. Heat Exchanger according to claim 6, wherein the tubes of the third bundle placed in the middle are of low alloy steel and the baffles and rods holding the baffles in place and the walls of the middle bundle are of temperature and corrosion resistant alloy.

10. Heat exchanger according to claim 5, wherein the wall separating the heating zones is of metal and is positioned to divide the flow of the second fluid into several streams by passage through openings in the wall.

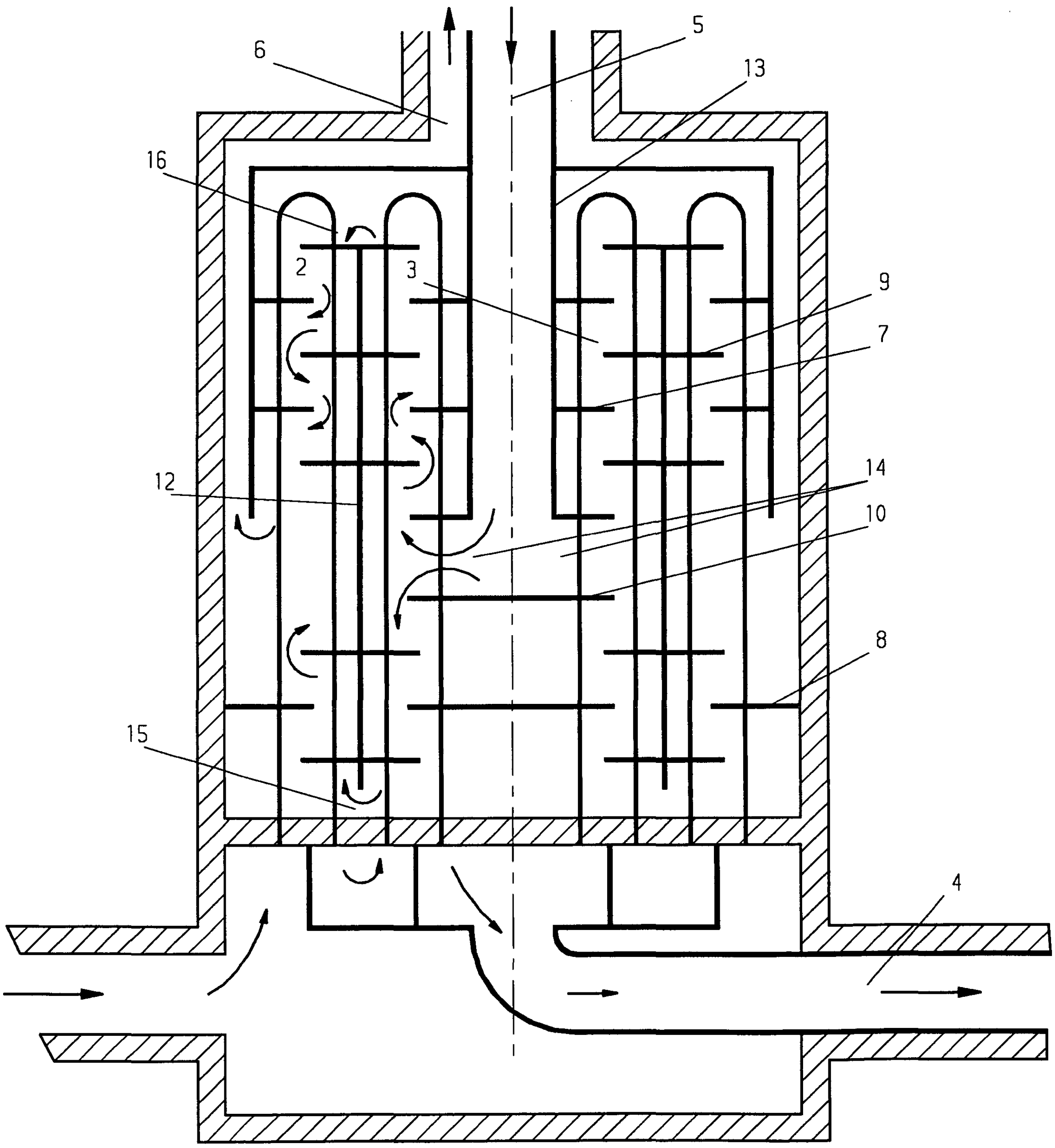

FIG. 1

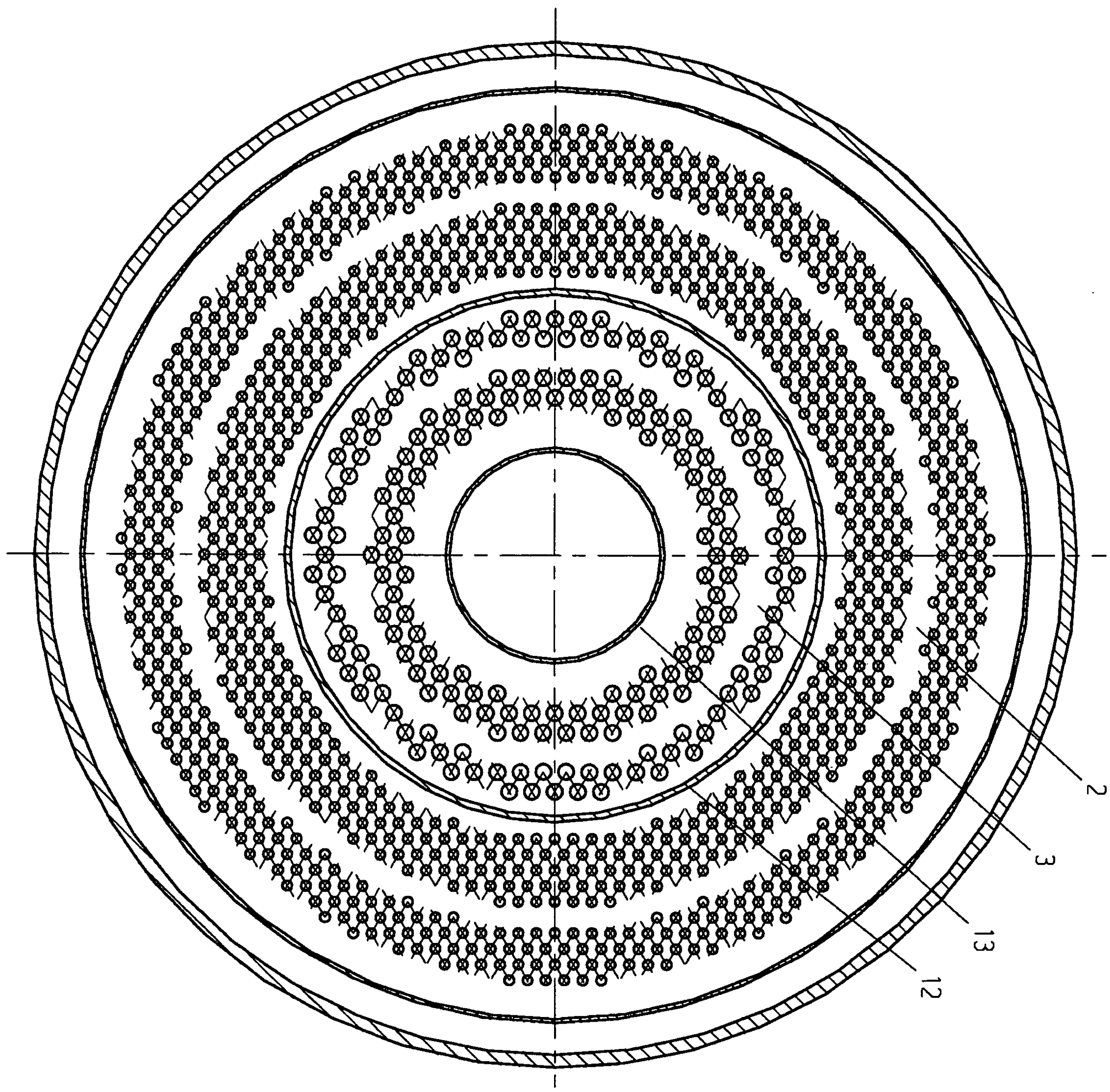

FIG. 2

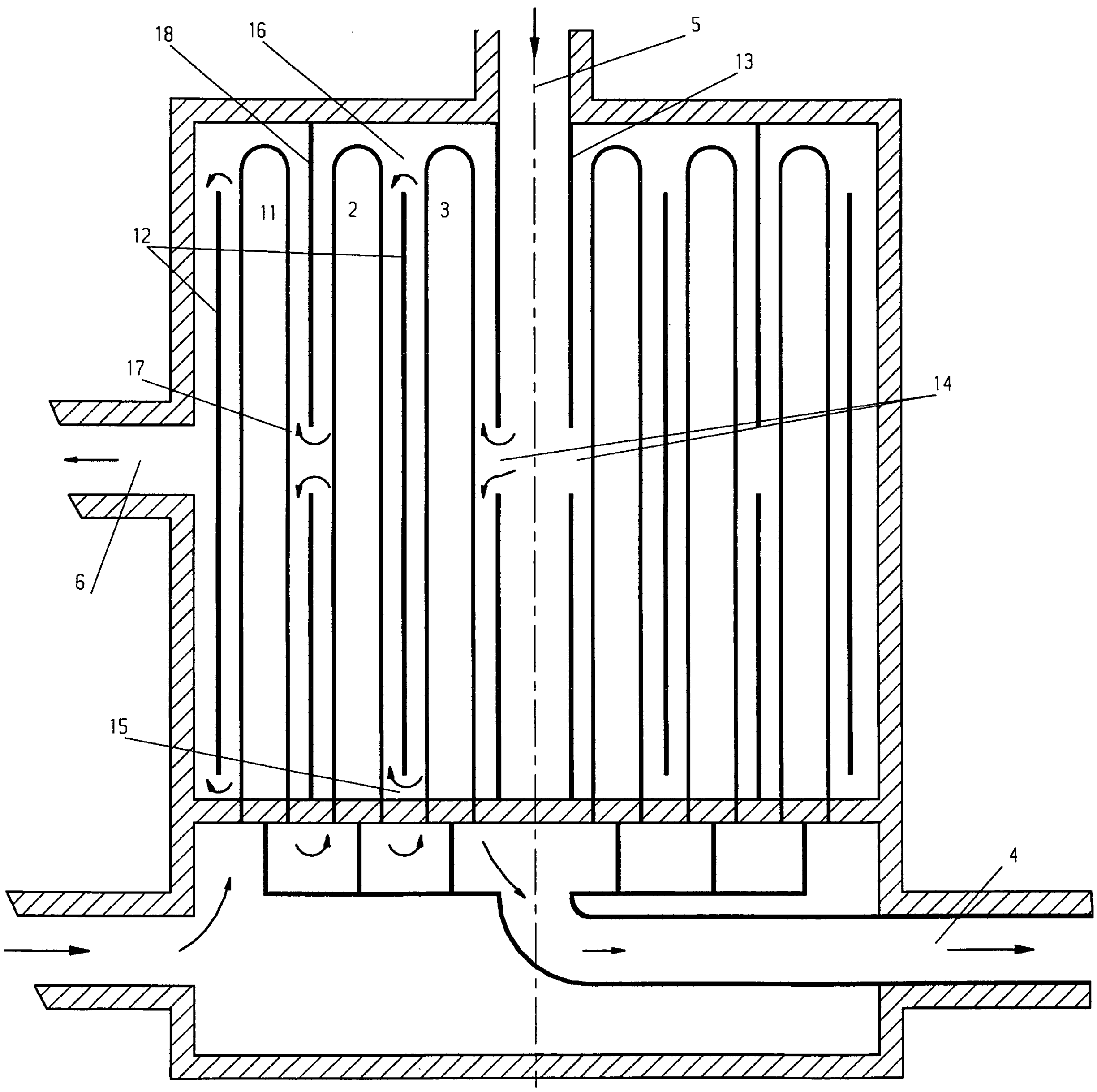

FIG. 3

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EUROPEAN SEARCH REPORT

Application Number
EP 05 01 3053

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	US 2 774 575 A (WALTER HELLMUTH) 18 December 1956 (1956-12-18) * column 1, lines 15-30 * * column 3, line 70 - column 4, line 73; figures 5,6 *	1-10	F28D7/06 F28D7/00 F28F9/22 F28F21/08
Y	EP 0 390 420 A (C F BRAUN INC) 3 October 1990 (1990-10-03) * column 2, lines 2-50; figures 2-4 *	1-10	
A	EP 1 273 866 A (TAMURA, TETSUTO) 8 January 2003 (2003-01-08) * paragraph [0040] *	1,3,5,7, 9	
A	US 2003/213854 A1 (STICKFORD GEORGE H ET AL) 20 November 2003 (2003-11-20) * paragraphs [0005], [0006], [0035]; claims 1-3 *	1,5	
A	US 6 623 869 B1 (NISHIYAMA YOSHITAKA ET AL) 23 September 2003 (2003-09-23) * the whole document *	2-4,7	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	US 6 153 152 A (RUHL ET AL) 28 November 2000 (2000-11-28) * column 16, lines 1-14 *	2-4,7	F28D F28F
A	US 2002/155061 A1 (PRASAD RAVI ET AL) 24 October 2002 (2002-10-24) * paragraph [0023] *	2-4,7	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	31 August 2005	Leclaire, T

CATEGORY OF CITED DOCUMENTS

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 05 01 3053

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31-08-2005

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 2774575	A	18-12-1956	NONE			
EP 0390420	A	03-10-1990	US	4907643	A	13-03-1990
			AU	611377	B2	06-06-1991
			AU	5211890	A	27-09-1990
			CA	2012673	A1	22-09-1990
			DE	69009267	D1	07-07-1994
			DE	69009267	T2	08-09-1994
			EP	0390420	A1	03-10-1990
EP 1273866	A	08-01-2003	JP	3509695	B2	22-03-2004
			JP	2001296014	A	26-10-2001
			EP	1273866	A1	08-01-2003
			US	2003106328	A1	12-06-2003
			CN	1422377	A	04-06-2003
			WO	0179775	A1	25-10-2001
US 2003213854	A1	20-11-2003	NONE			
US 6623869	B1	23-09-2003	JP	2003073763	A	12-03-2003
			CA	2420010	A1	17-02-2003
			CN	1463296	A ,C	24-12-2003
			EP	1403392	A1	31-03-2004
			WO	02103072	A1	27-12-2002
			ZA	200300919	A	19-08-2003
US 6153152	A	28-11-2000	AU	661877	B2	10-08-1995
			AU	3026492	A	18-02-1993
			US	6096106	A	01-08-2000
			US	5567398	A	22-10-1996
			US	5565009	A	15-10-1996
			AT	178221	T	15-04-1999
			BR	9205058	A	30-11-1993
			CA	2079746	A1	20-06-1993
			CN	1075790	A ,C	01-09-1993
			DE	69228834	D1	06-05-1999
			DE	69228834	T2	05-08-1999
			DK	643618	T3	11-10-1999
			EP	0643618	A1	22-03-1995
			ES	2129513	T3	16-06-1999
			FI	942930	A	17-06-1994
			GR	3029840	T3	30-07-1999
			JP	5269369	A	19-10-1993
			MX	9207371	A1	01-12-1993
			NO	942277	A	16-06-1994
			NZ	245475	A	27-02-1996

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 05 01 3053

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31-08-2005

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6153152 A		RU 2134154 C1	10-08-1999
		WO 9312032 A1	24-06-1993
		KR 241568 B1	01-02-2000
		ZA 9209730 A	22-06-1993
		AT 114253 T	15-12-1994
		AU 698930 B2	12-11-1998
		AU 3777495 A	18-01-1996
		AU 7356491 A	19-12-1991
		BR 9101266 A	26-11-1991
		CA 2038289 A1	04-10-1991
		DE 69105230 D1	05-01-1995
		DK 450872 T3	12-12-1994
		EP 0450872 A1	09-10-1991
		JP 3075757 B2	14-08-2000
		JP 5096149 A	20-04-1993
		KR 170398 B1	15-01-1999
		ZA 9101838 A	24-12-1991
US 2002155061 A1	24-10-2002	BR 0209225 A	20-07-2004
		CA 2445484 A1	19-12-2002
		CN 1520377 A	11-08-2004
		EP 1390291 A1	25-02-2004
		JP 2005503980 T	10-02-2005
		NO 20034752 A	18-12-2003
		WO 02100773 A1	19-12-2002
		ZA 200308235 A	26-07-2004

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82