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(54) Title: METHOD FOR THE SEPARATION OF AT LEAST ONE PREDETERMINED ELEMENT FROM THE MATERIAL INVOLVED IN AN INDUSTRIAL PROCESS AND RELATIVE PLANT

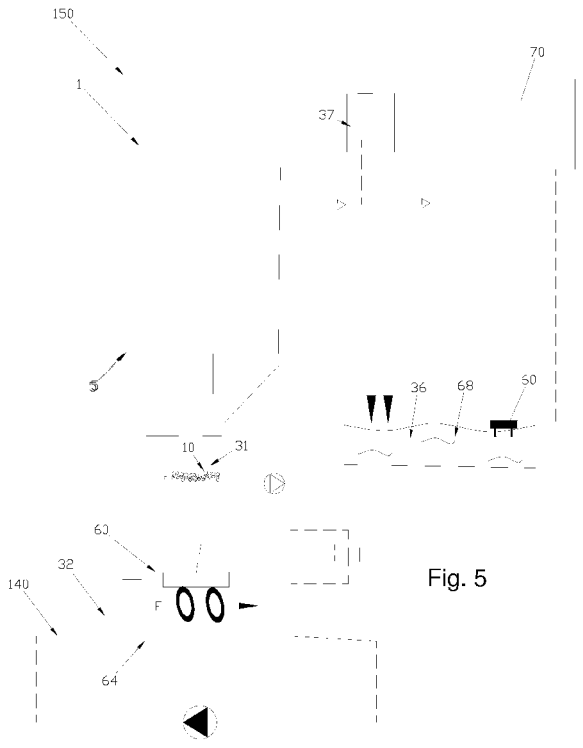

Fig. 5

(57) Abstract: The present invention concerns a method for separating at least one predetermined element from the material involved in an industrial process, characterised in that said industrial process is associated in loco with an electrocapturing process by electrolysis of said at least one element.

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METHOD FOR THE SEPARATION OF AT LEAST ONE PREDETERMINED ELEMENT FROM THE MATERIAL INVOLVED IN AN INDUSTRIAL PROCESS AND RELATIVE PLANT.

* * * * *

DESCRIPTION

Method for separating at least one predetermined element from the material involved in an industrial process and relative plant. The present invention has been developed with particular reference to the field of recycling and reclamation, and especially to the treatment of the residues of the waste thermolysis process, in particular for the extraction of valuable elements from it, like for example metals. However, this does not rule out other applications, especially those in association with industrial plants with production of electrical energy or of fuels able to be used *in loco* for the production of electrical energy.

Thermolysis is known to be a treatment process of organic waste consisting of industrial, agricultural or domestic waste to dispose of it. This process is an endothermal chemical reaction that causes the rupture of the chemical bonds.

The residue of the thermolysis process is very rich in valuable elements, like for example carbon, gas and pyrolysis oil, which are recovered for use as fuels,

or as metals, which are separated for reuse in industry. The process is also able to produce vapour from which to generate electric current.

An example of a plant for the thermolysis of organic waste id described in patent application FR0309592 (publication number FR2858570) to POULLEAU GERARD and others. The plant is shown in summary in figure 1 (corresponding to figure 2 of such a patent application and used purely for comparison).

In such a thermolysis plant, indicated with reference numeral 1, there is a furnace 5, where the thermolysis of the waste is carried out at a temperature comprised between 600°C and 1100°C, and an exhaust pipe 31, where the residue 10 of the thermolysis process comes out at a temperature comprised between 500°C and 850°C.

The plant 1 also comprises a device 37 for collecting the gases produced in the furnace 5, as well as various devices for separating the components that form the residue 10.

Known separation devices in particular comprise, downstream of the furnace 5, a washing tank 32 of the residue 10, where the carbon 12 is separated by floating and the heavy elements 14 by depositing on the bottom.

The carbon is then removed with a dripping conveyor belt 34, arranged above a percolate collection tank.

The heavy residues, on the other hand, are evacuated through a duct 33, and the metals present are separated and recovered through the application of "Foucault currents".

The washing water and the percolate are sent to a decanting tank 36.

It should be noted that the separation of the metals through Foucault currents is a known type of selection of recycled metals that exploits magnetism. However, it is known and effective mainly for separating aluminium from ferrous materials, and it has some difficulties of application to the residue in question, rich in very many types of valuable materials to be recovered. Moreover, it is not applicable to materials that remain trapped in the washing water, in the percolate and in the decanting water.

Therefore, if nothing else, there is still the problem of optimising the collection for recycling of valuable elements of the residue and of purifying the water and/or the liquids used in the plant. Indeed, they inevitably end up polluting aquifers, seas and rivers, with serious repercussions on human health.

Other industrial processes that could benefit from a separation of elements are, if no other, all those of the food industry, starting from the production of water and drinks, and those involved in the

pharmaceutical industry.

Amongst the most polluting elements that it would be useful to separate we note, in a non-exhaustive list, Cadmium, Lead, Mercury, Aluminium, Antimony, Arsenic, Tin, Thallium and Uranium, many of which are in metallic form.

These elements, as well as entering our body directly when water is drunk, are taken on through the food chain. A classic example is the concentration mechanism in fish or in acquaculture products that we eat on a daily basis.

Amongst the numerous bibliographic references that we could quote to quantify the extent of pollution of water on the planet and the impact on man we note the following very complete report: ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA, July 1, 1997; COMPILERS/EDITORS: ROY J. IRWIN, NATIONAL PARK SERVICE; WITH ASSISTANCE FROM COLORADO STATE UNIVERSITY; STUDENT ASSISTANT CONTAMINANTS SPECIALISTS: MARK VAN MOUWERIK, LYNETTE STEVENS,MARION DUBLER SEESE, WENDY BASHAM, NATIONAL PARK SERVICE WATER RESOURCES DIVISIONS, WATER OPERATIONS BRANCH; 1201 Oakridge Drive, Suite 250, FORT COLLINS, COLORADO 80525.

As can be seen, the aforementioned report is from 1997, and yet other previous ones could be given, to demonstrate the fact that the problem has been around for

a very long time.

Moving on to the aspect of oncological research, a recent study of the university of Ferrara offered a complete summary of the damage caused in the body by these pollutants: *3.7.2013 Prof. Francesco Caritei, University of Ferrara, Inquinamento della fauna ittica e delle acque da metalli pesanti e conseguenze sanitarie nell' uomo; in particolare in campo oncologico.*

The fact that such a report was only a few days prior to the filing date of the present patent application demonstrates the absence of a radical solution to the problem.

It has thus been demonstrated that in current society for many years, there has been a need to find global systems that are applicable on a large scale to reduce the pollution of our planet's water and food.

A general purpose of the present invention is therefore to at least partially overcome the problems indicated above and/or to at least partially satisfy the quoted needs.

A preferred purpose of the present invention is to provide a method for making the recycling of the elements involved in an industrial process efficient, and at the same time to reduce the pollution of the water used in such a process.

A further preferred purpose of the present

invention is to optimise the waste treatment process by thermolysis, getting value from the residue.

A further preferred purpose of the present invention is to provide a method that is easy and cost-effective to make.

According to a first general aspect thereof, the present invention concerns a method for separating at least one predetermined element from the material involved in an industrial process where said industrial process is associated *in loco* with at least one electrocapturing process by electrolysis of said at least one element. When needed, it is also possible to generate electrolytic dissociation to generate the ions of said element to be captured through electrocapturing.

The method can advantageously be applied to any polluting and/or valuable element that can have an ionic form, like for example metals and salts.

The following non-exhaustive table shows some polluting and/or valuable elements that can be captured with the method of the present invention:

Element
Li
Mo
U
V
Cd
Au
Sn
Ni
Cu
Mn
Zn
Al
Cr
Pb
Fe
Ti
Co

The capture is preferably selective, for example the selection can be differentiated and/or can vary over time.

This can easily be obtained when the electrocapturing phenomenon comprises at least one electrodeposition phenomenon on at least one electrode.

The electrodes can, indeed, be supplied with amperage or potential difference values such as to select the element, or more than one, to be captured, and such values are easily set through a programmable control station.

The variable selection over time could be advantageous to adapt the electrocapturing process to the variation over time of the material involved in the industrial process. According to some preferred embodiments, the selection varies over time as a function of at least one detected characterising parameter of said material.

According to a general preferable characteristic of the invention the electrocapturing process is

electrically powered by the electric current produced directly by the industrial process with which it is associated or from that produced *in loco* with at least one material produced by the industrial process with which it is associated, or by that produced *in loco* exploiting at least one renewable energy source.

According to another general preferable characteristic a predetermined liquid compound is made comprising at least part of said material involved in the industrial process and the electrocapturing process is applied at least to said compound.

Some embodiments that are particularly advantageous due to their high productivity foresee the step of artificially generating the mobility of said material in the liquid compound during the electrocapturing process.

This can be achieved easily in various ways, for example in the form of ionic mobility, stimulated by a supply of the electrocapturing process with variable parameters over time (governed preferably by a station). For example, it is possible to use a variable power current, for example in pulses, and/or a variable potential difference, for example in pulses. Nevertheless, this does not rule out, additionally or alternatively, an agitation of the liquid compound, for example mechanically, for example by mixing.

According to some preferred embodiments, the industrial process with which the electrocapturing process is associated is a waste treatment process by thermolysis that produces a thermolysis residue. The liquid compound is therefore formed with at least part of the residue.

According to a second general aspect thereof, the present invention comprises a plant for separating at least one predetermined element from the material involved in an industrial process through the application of a method of the type indicated above.

Preferably, the plant comprises at least one annular or substantially annular electrode. This can be advantageously exploited in various ways.

For example, the annular electrode can be made to rotate with respect to a scraping device (and vice-versa, to collaborate in the removal of the at least one type of predetermined element captured.

Thanks to this, the electrolysis process can be carried out continuously, i.e. without stopping to take out the captured elements from the electrodes, with a great advantage for the productivity and ability to be associated with any industrial process. The rate of the latter does not, indeed, need to be reduced to proportion it to the purification times of the electrolysis.

Another example of advantageous exploitation is

the positioning of many annular electrodes to form a flow channel for said liquid compound, so as to increase the efficiency of collection.

Further characteristics and advantages of the present invention will become clearer from the following detailed description of preferred embodiments thereof, made with reference to the attached drawings and given for indicating and not limiting purposes. In such drawings:

- figure 1 is a schematic representation of a known industrial plant for carrying out a waste treatment process by thermolysis;

- figure 2 is a schematic representation of the same plant with which some electrocapturing units by electrolysis have been associated;

- figure 3 is a schematic representation of a module for electrocapturing according to the present invention, and

- figure 4 is a schematic representation of a device for collecting the materials captured by electrolysis.

With reference to figure 2, a plant is shown according to the present invention indicated in general with reference numeral 50, which coincides with the plant 1 of figure 1 equipped with some electrocapturing units by electrolysis, indicated in general with reference

numeral 60, and a generator of electric current *in loco* 70.

As can be noted, the electrocapturing units 60 can be applied in any point of the plant in which there is a liquid compound 64, 66 and 68, rich in elements to be extracted, like for example those of the previous table.

The compounds in general comprise, as liquid fraction, water and possible liquid residues deriving from the industrial process, however this does not rule out the possibility, in association with or as an alternative to water, of using other liquids. For example, the compound 64 is given by the washing water and by the thermolysis residue 10. It should be observed that the thermolysis residue comes out from the furnace at a temperature of between 500°C and 850°C, hence it causes the evaporation of the water. A first solution to this problem can be that of carrying out the electrolysis in the boiling compound 64 gradually replacing the water that evaporates. In this case it is preferable to use carbon electrodes, since they withstand heat better. It is also possible to filter the vapour produced with at least one microporous membrane 72 capable of holding the residues of predetermined elements possibly contained in the vapour. The membranes 72 can be selective.

Additionally or alternatively it is possible to

cool the residue 10 before forming the compound 64 and/or alter the pressure conditions, for example by increasing the pressure of the electrolysis environment to reduce evaporation.

In general, the modules for electrolysis 60 comprise at least one electrolytic cell, i.e. at least one pair of electrodes fed in current to act as anode and cathode in the electrolytic process.

With reference to figure 3, an example of an electrolytic module 60 is illustrated, where the electrodes 80 are annular in shape. They are arranged facing one another to form a flow channel 85 for the liquid compound, where the flow is indicated by the arrow F.

The module 60 can be equipped with a device 90 for collecting the elements captured by the electrodes, schematically illustrated in figure 4. Such a device is a scraper that scrapes on the surface of the electrodes 80 while they rotate (arrow R) about their axis X. The rotation axis X coincides with the axis about which the annular electrodes 80 develop by revolution.

A man skilled in the art will realise that a generic electrocapturing module comprising at least one annular electrode with a scraping device like the one illustrated can also form the object of an independent invention from the one illustrated, since it is

applicable to any electrolysis process.

The module 60 comprises, and/or is connected to a control station 95 of the power supply parameters of the electrodes 80. The station is programmed to set predetermined power supply parameters for each type of element that it is intended to capture. The selection of the type of element to be captured can be done manually, or automatically through a feedback system that comprises a device 97 for analysing the composition of the liquid compound. For example, it is possible to set the station so that it orders the capture of a certain element when its concentration is above a predetermined threshold value.

Figure 5 shows an alternative embodiment of the plant 50, indicated with reference numeral 150, where elements that are the same or similar are indicated with the same reference numerals used previously or increased by 100 or by a multiple thereof.

The plant 150 comprises, downstream of the furnace 5, a capturing station by electrolysis in which there is a recirculation circuit 140 of the compound 64, so that it can pass many times through the channel 85, or through a plurality of channels 85.

In use, the plants 50 and 150 foresee making a thermolysis process of waste in the furnace 5 from which gases 8 and residue 10 are formed.

The gases are sent to the power station 70 to generate the power supply current of one or more modules 60 of the plant.

The residue 10 is dissolved in water to form at least the compound 64, in a collection tank 32 or in a recirculation circuit 140, in which the electrocapturing by electrolysis and the collection of the elements thus separated from the compound 64 takes place. The thermolysis and electrocapturing operations can take place simultaneously and continuously.

In general, the liquid compound in which the electrolysis is carried out, can have elements associated with it that increase the conductivity of the solution, like for example sodium chloride, the liquid fraction (or solvent) of the compound, as already stated, can be water and/or another type of liquid.

Of course, the embodiments and the variants described and illustrated up to now are purely examples and a man skilled in the art, in order to satisfy specific and contingent requirements, can bring numerous modifications and variants, including for example the combination of said embodiments and variants, all in any case covered by the scope of protection of the present invention as defined by the following claims.

CLAIMS

1. Method for separating at least one predetermined element from the material involved in an industrial process, characterised in that said industrial process is associated *in loco* with an electrocapturing process by electrolysis of said at least one element.

2. Method according to claim 1, characterised in that said electrocapturing phenomenon comprises at least one electrodeposition phenomenon on at least one electrode (80).

3. Method according to any one of the previous claims, characterised in that a selective electrocapturing process of a plurality of predetermined elements is carried out.

4. Method according to the previous claim, characterised in that the selective electrocapturing is a differentiated electrocapturing.

5. Method according to claim 3 or 4, characterised in that the selection varies over time, for example as a function of at least one detected characterising parameter.

6. Method according to any one of the previous claims, characterised in that the electrocapturing process is powered electrically by the electric current produced directly by the industrial process with which it

is associated or by that produced *in loco* with at least one material produced by the industrial process with which it is associated, or from that produced *in loco* by exploiting at least one renewable energy source.

7. Method according to any one of the previous claims, characterised in that it comprises the step of making a predetermined liquid compound (64, 66, 68) comprising at least part of said material (10) involved in the industrial process and of applying the electrocapturing process at least to said compound.

8. Method according to the previous claim, characterised in that it comprises the step of artificially generating the mobility of said material (10) in the liquid compound (64, 66, 68) during the electrocapturing process.

9. Method according to the previous claim, characterised in that said step of generating the mobility comprises the generation of an ionic mobility stimulated by a supply of the electrocapturing process with parameters that are variable over time, for example it is possible to use a supply current with variable amperage, for example in pulses, and/or a variable potential difference, for example in pulses.

10. Method according to claim 8 or 9, characterised in that said step of generating the mobility comprises the step of agitating said liquid

compound (64, 66, 68).

11. Method according to any one of claims 7 to 10, characterised in that it comprises the step of carrying out the electrocapturing process at a condition of such a compound (64, 66, 68) below the boiling condition.

12. Method according to any one of claims 7 to 11, characterised in that before making such a liquid compound (64, 66, 68) it comprises the step of reducing the temperature of said at least part of the material involved (10) to a temperature below the boiling temperature of the liquid phase of said liquid compound (64, 66, 68) considered in the pressure conditions at which the electrocapturing process takes place.

13. Method according to any one of claims 7 to 12, characterised in that the electrocapturing process is carried out at a temperature above room temperature and the liquid fraction of the compound that evaporates is at least partially replaced.

14. Method according to claim 13, characterised in that the vapour of the liquid fraction is filtered with at least one selective membrane to hold at least one type of possible predetermined elements.

15. Method according to any one of claims 7 to 14, characterised in that the industrial process is a waste treatment process by thermolysis and produces a

thermolysis residue, where said liquid compound is formed with at least part of said residue.

16. Plant for separating at least one predetermined element from the material involved in an industrial process through the application of a method according to any one of the previous claims, characterised in that it comprises a plant for carrying out such an industrial process with which at least one electrocapturing unit by electrolysis is associated.

17. Plant according to the previous claim, characterised in that it comprises at least one electrode having an annular or substantially annular shape.

18. Plant according to the previous claim, characterised in that such an at least one electrode develops around an axis of revolution in an annular shape, the plant comprising a device for removing the at least one type of predetermined element from said at least one circular electrode by scraping the electrode itself.

19. Plant according to the previous claim, characterised in that the annular electrode and/or the scraping device rotate with respect to one another around the axis of development by revolution of the electrode.

20. Plant according to any one of claims 17 to 19, characterised in that it comprises a plurality of annular or substantially annular electrodes that form a

flow channel for said liquid compound.

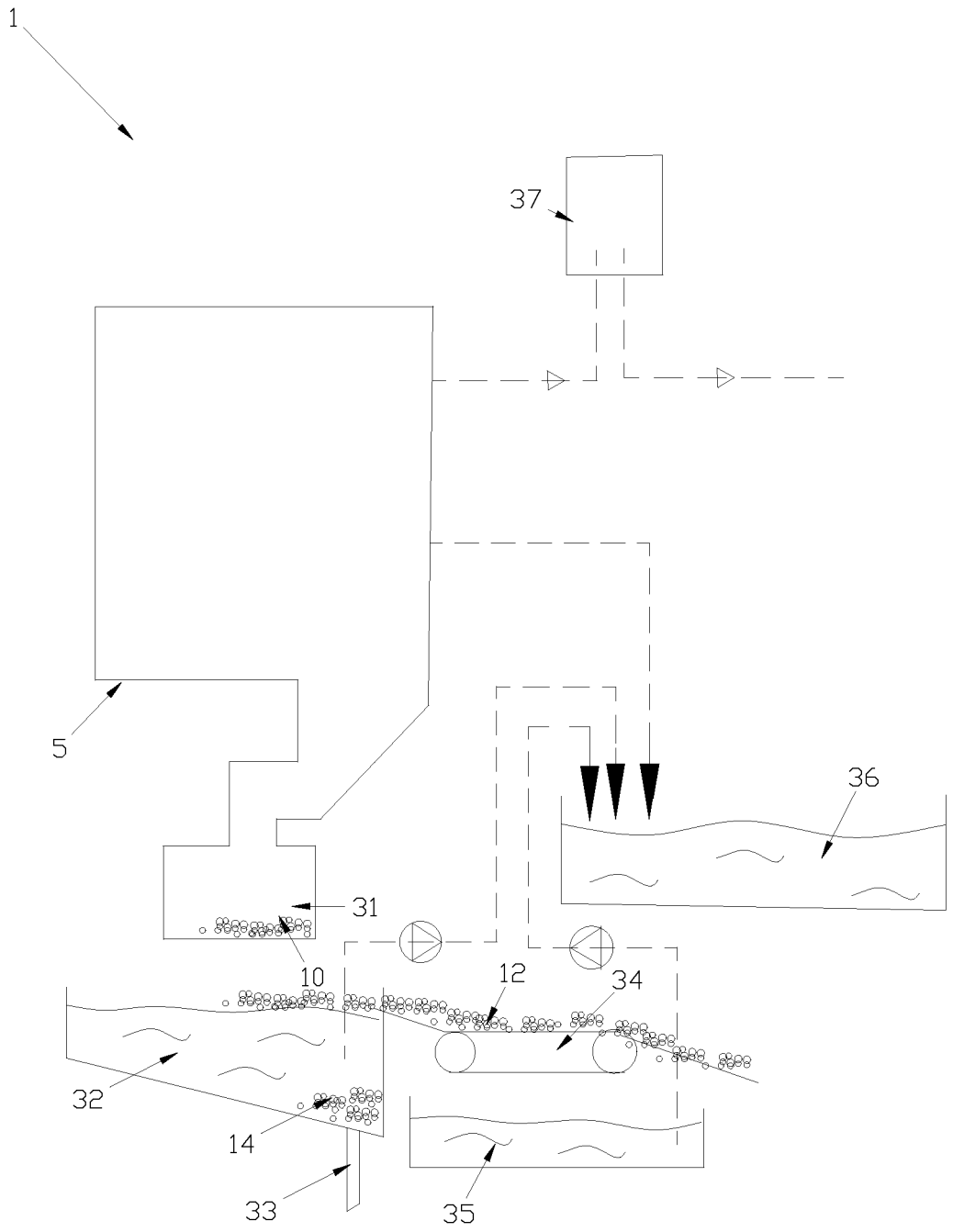

Fig. 1

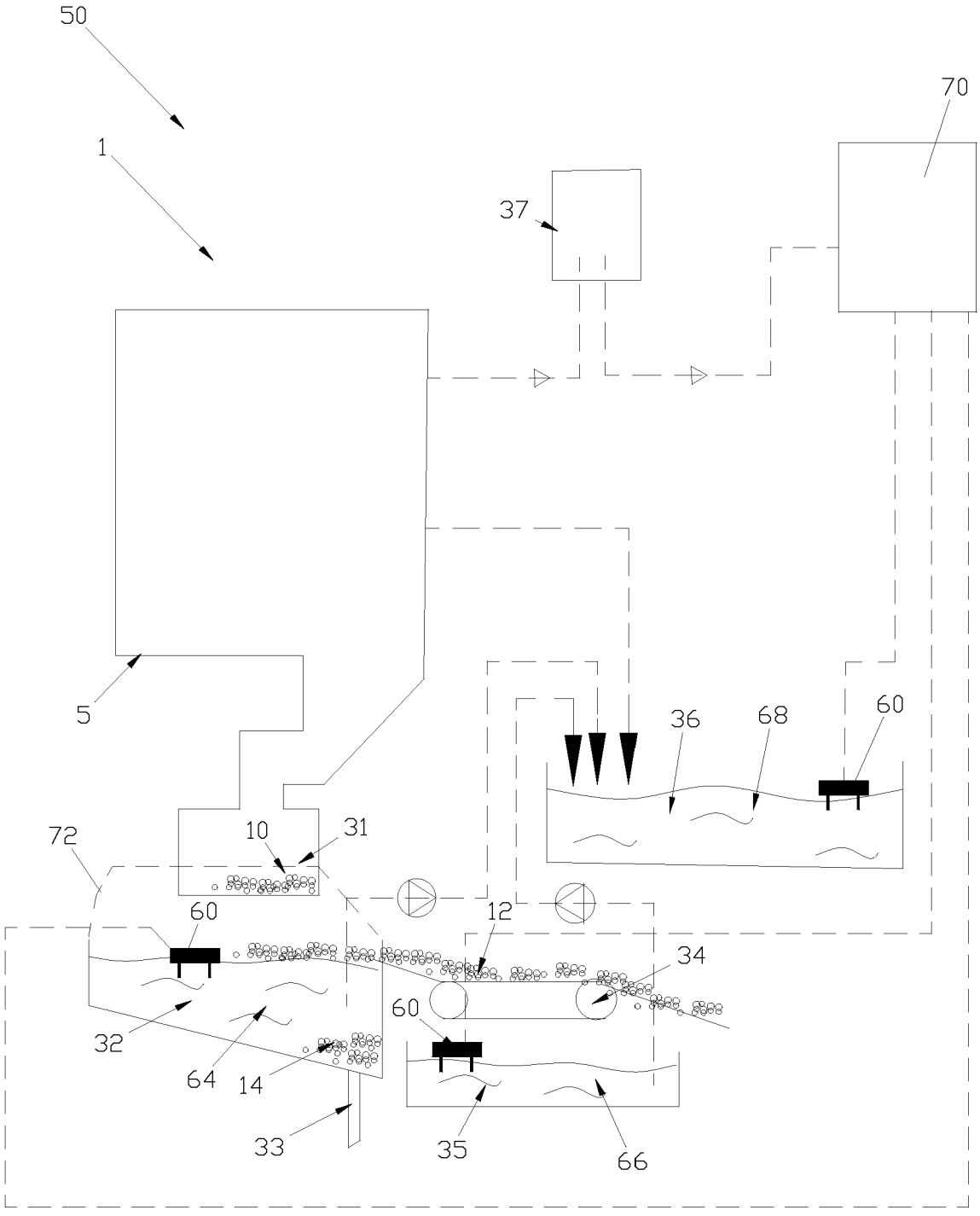

Fig. 2

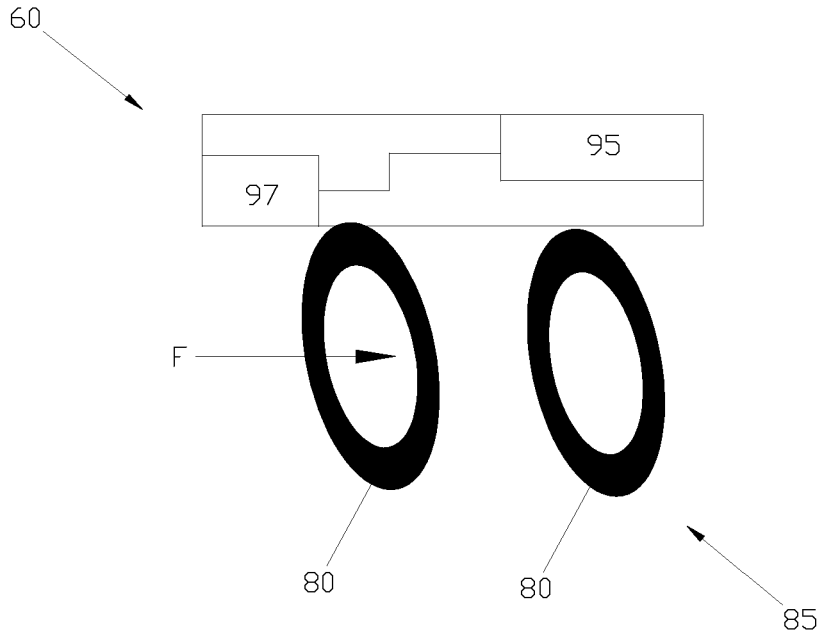

Fig. 3

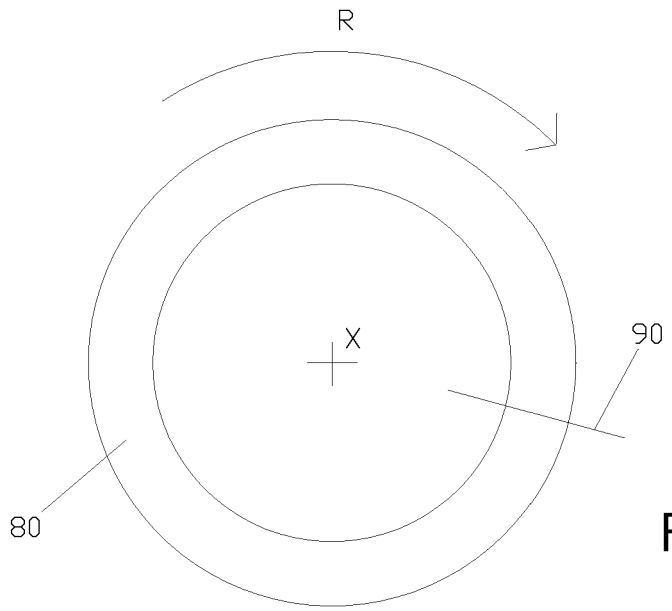

Fig. 4

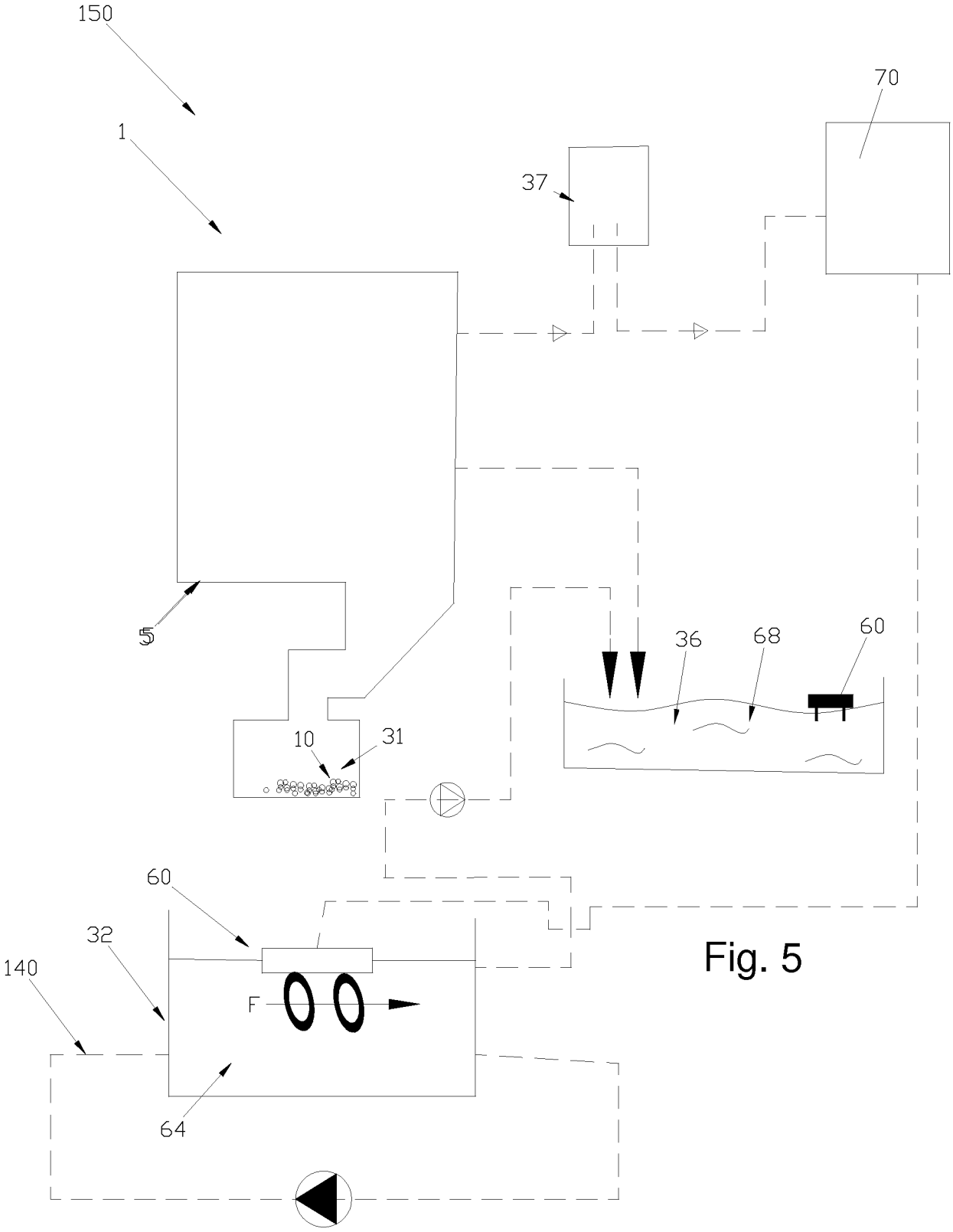

Fig. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2013/056397

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25C1/00 C02F1/461
ADD.

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)
C25C C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 549 067 A2 (HOOGOVENS GROEP BV [NL]) 30 June 1993 (1993-06-30) column 5, lines 6-54 column 11, lines 21-24 column 11, line 41 - column 12, line 22; figure 3	1,2,5-7, 11-16
X	EP 2 388 305 A2 (TERRANOVA ENERGY GMBH [DE]) 23 November 2011 (2011-11-23) paragraphs [0037], [0045], [0050], [0074] - [0088], [0113] - [0120]	1,3-7, 15,16
X	US 2006/243595 A1 (HENUSET YVES M [CA] ET AL) 2 November 2006 (2006-11-02) paragraphs [0003], [0010], [0060], [0061], [0069], [0081], [0083]; example 2	1-4, 7-10,16, 17,20

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 November 2013	12/12/2013

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2013/056397

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 406 753 A (BLAKE COLIN C [GB] ET AL) 27 September 1983 (1983-09-27) the whole document -----	1,16-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2013/056397

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0549067 A2	30-06-1993	AT 125240 T	15-08-1995
		CA 2085942 A1	24-06-1993
		DE 69203588 D1	24-08-1995
		DE 69203588 T2	11-01-1996
		DK 0549067 T3	11-09-1995
		EP 0549067 A2	30-06-1993
		ES 2074816 T3	16-09-1995
		GR 3017359 T3	31-12-1995
		NL 9102168 A	16-07-1993
EP 2388305 A2	23-11-2011	NONE	
US 2006243595 A1	02-11-2006	NONE	
US 4406753 A	27-09-1983	DE 3362365 D1	10-04-1986
		EP 0084521 A2	27-07-1983
		US 4406753 A	27-09-1983