US 20140352912A1

(19) **United States**

(12) **Patent Application Publication**

Francy

(10) **Pub. No.: US 2014/0352912 A1**

(43) **Pub. Date: Dec. 4, 2014**

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(54) **REGENERATOR**

(71) Applicant: **Saint-Gobain Centre De Recherches Et D' Etudes Europeen**, Courbevoie (FR)

(72) Inventor: **Olivier Francy**, L' Isle Sur La Sorgue (FR)

(21) Appl. No.: **14/367,787**

(22) PCT Filed: **Dec. 20, 2012**

(86) PCT No.: **PCT/IB2012/057507**

§ 371 (c)(1),
(2), (4) Date: **Jun. 20, 2014**

(30) **Foreign Application Priority Data**

Dec. 22, 2011 (FR) 1162272

Publication Classification

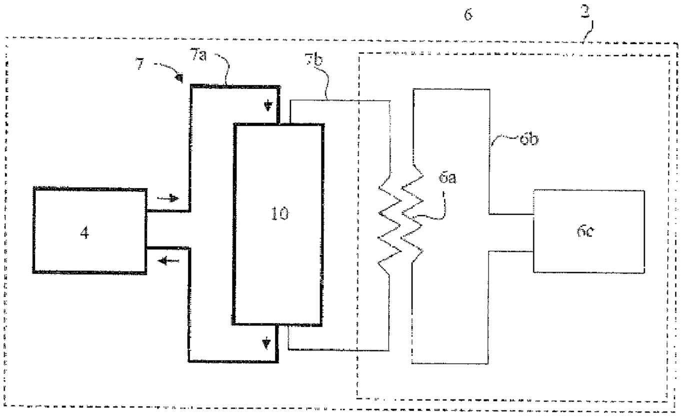
(51) **Int. Cl.**
F28D 17/02 (2006.01)

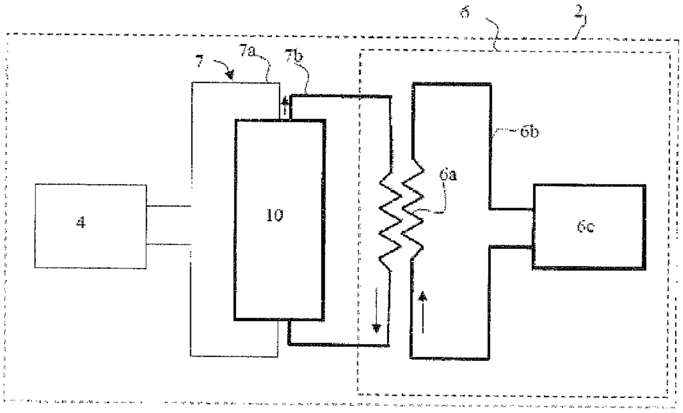
(52) **U.S. Cl.**
CPC *F28D 17/02* (2013.01)
USPC **165/10**

(57) **ABSTRACT**

The present invention relates to a regenerator comprising a bed (**11**) of energy storage media (**12**) placed in a chamber (**14**), the chamber comprising a shell (**34**) and a protective layer (**22**) placed between said shell and said energy storage media, in contact with said energy storage media, having a minimum thickness higher than 50 mm and consisting, at least partially, of a protective material having a composition, in weight percent based on the oxides, such that:

$Fe_2O_3+Al_2O_3+CaO+TiO_2+SiO_2+Na_2O+K_2O>80\%$, and other oxides: complement to 100%.





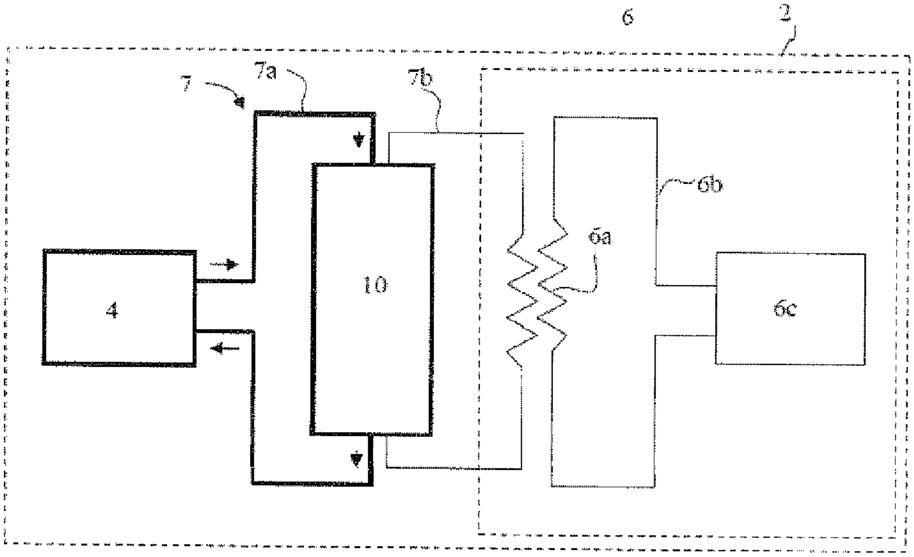


Fig. 1a

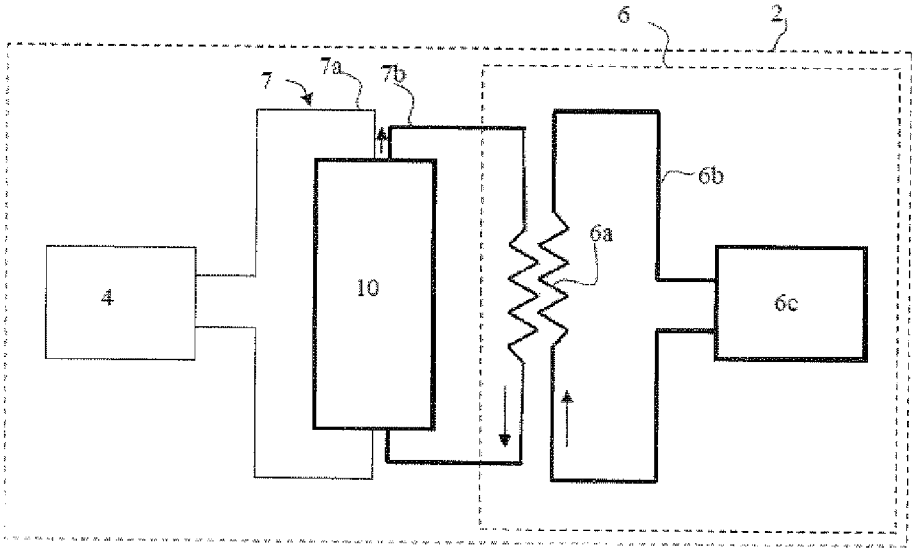


Fig. 1b

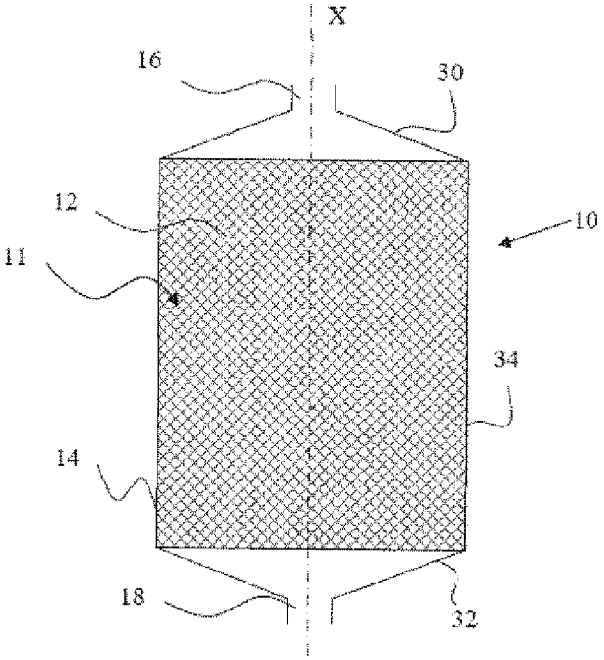


Fig. 2

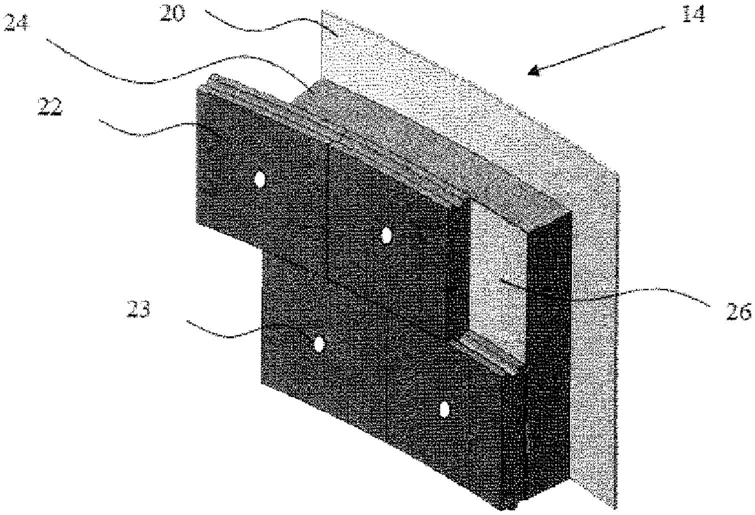


Fig. 3

REGENERATOR

TECHNICAL FIELD

[0001] The invention relates to a thermal storage regenerator, and to a thermal installation comprising such a regenerator.

TECHNOLOGICAL BACKGROUND

[0002] The storage of energy, for example heat energy, serves to shift the production and consumption of said energy in time.

[0003] Heat energy storage is also useful for utilizing soft energies, such as solar energy, which are renewable but are produced intermittently. Energy storage can also be useful for exploiting differences in electricity prices between off-peak hours, during which the electricity tariffs are the lowest, and peak hours, during which the tariffs are the highest. For example, in the case of compressed air energy storage, generating heat energy which is stored in a thermal regenerator, the compression phases consuming electricity are advantageously carried out at minimum cost during off-peak hours, while the expansion phases producing electricity are carried out during peak hours, in order to supply electricity which can be injected into the grid, in accordance with demand, at an advantageous tariff.

[0004] The heat energy is conventionally stored in a packed bed of energy storage media of a regenerator, for example in a pebble bed.

[0005] The storage operation, by heat exchange between a stream of heat transfer fluid and the regenerator, is conventionally called the charge phase, the heat transfer fluid entering the regenerator during the charge being called the charge heat transfer fluid.

[0006] The transfer of heat energy can cause an increase in the temperature of these energy storage media (sensible heat storage) and/or a phase change of these media (latent heat storage).

[0007] The heat energy stored can then be restored, by heat exchange between a stream of heat transfer fluid and the energy storage media. This operation is conventionally called the discharge phase, the heat transfer fluid entering the regenerator during the discharge is called discharge heat transfer fluid, and the time elapsed between the end of the charge phase and the beginning of the discharge phase is called the storage time.

[0008] "*A review on packed bed solar energy storage systems*", Renewable and Sustainable Energy Reviews, 14 (2010), p 1059-1069, describes the prior art in the field of regenerators.

[0009] During the operation of a regenerator, and in particular when a heat transfer fluid is humid air, the condensates of the moisture in the air corrode the regenerator materials. Furthermore, at high pressures, the moisture present in the air can condense and mix with the other condensates or pollutants present. The latter can then make the water acidic and therefore corrosive. This causes a considerable decrease in the service life of the regenerator, which should be longer than 20 years, or even longer than 30 years in industrial installations, and therefore an increase in the total cost.

[0010] A need therefore exists to increase the service life of the regenerators, in particular with regard to corrosive acidic attack, particularly at operating temperatures higher than 350° C., or even higher than 500° C., and in particular for regenerators charged with humid air.

[0011] It is an object of the invention to meet this need, at least partially.

SUMMARY OF THE INVENTION

[0012] This object is achieved using a regenerator, in particular a sensible heat regenerator, comprising a bed of energy storage media placed in a chamber, the chamber comprising a shell and a protective layer placed between said shell and said energy storage media, in contact with said energy storage media, having a minimum thickness higher than 50 mm and consisting, at least partially, and preferably entirely, of a protective material having a composition, in weight percent based on the oxides, such that:

[0013] $Fe_2O_3+Al_2O_3+CaO+TiO_2+SiO_2+Na_2O+K_2O>80\%$, and

[0014] other oxides: complement to 100%.

[0015] The inventors have found that a regenerator according to the invention has a longer service life, particularly in applications, according to the invention, in which the energy storage media are brought into contact with acidic liquids.

[0016] In a first embodiment, the composition of the material of the protective layer, or protective material, is preferably such that:

[0017] $Fe_2O_3+Al_2O_3+SiO_2>80\%$, preferably $Fe_2O_3+Al_2O_3+SiO_2>90\%$, and/or

[0018] $Al_2O_3>60\%$, preferably $Al_2O_3>85\%$, preferably $Al_2O_3>95\%$, and/or

[0019] $Fe_2O_3<20\%$, preferably $Fe_2O_3<10\%$, preferably $Fe_2O_3<3\%$, and/or

[0020] $SiO_2<10\%$, preferably $SiO_2<5\%$, preferably $SiO_2<2\%$, and/or

[0021] $CaO<2\%$, preferably $CaO<1\%$, preferably $CaO<0.5\%$, and/or

[0022] $Na_2O+K_2O<0.5\%$, preferably $Na_2O+K_2O<0.3\%$, preferably $Na_2O+K_2O<0.2\%$.

[0023] In a second embodiment, the composition of the protective material is preferably such that:

[0024] $25\%<Fe_2O_3<70\%$, preferably $Fe_2O_3>40\%$, and

[0025] $5\%<Al_2O_3<30\%$, preferably $Al_2O_3<20\%$, and

[0026] $CaO<20\%$, preferably $CaO>3\%$, and

[0027] $TiO_2<25\%$, preferably $TiO_2>5\%$, and

[0028] $3\%<SiO_2<50\%$, preferably $SiO_2>5\%$ and/or $SiO_2<20\%$, and

[0029] $Na_2O+K_2O<10\%$, preferably $Na_2O+K_2O<5\%$, and

[0030] other oxides<5%, preferably other oxides<3%.

[0031] Preferably, the protective material comprises a majority compound selected from the group consisting of alumina, bauxite, spinel $MgAl_2O_4$, mullite, hibonite $CaAl_{12}O_{19}$, aluminum titanate, and combinations thereof.

[0032] Even more preferably, the protective material has:

[0033] an open porosity lower than 20%, preferably lower than 10%, preferably lower than 5%, and

[0034] a compressive strength higher than 50 MPa, preferably higher than 70 MPa, preferably higher than 90 MPa, and

[0035] a pyroscopic resistance higher than 350° C., preferably higher than 700° C., preferably higher than 900° C.

[0036] Preferably, the minimum thickness of the protective layer is higher than 100 mm, preferably higher than 150 mm.

[0037] Preferably, the protective layer is run through by holes.

[0038] The protective layer further serves to place an insulating layer inside the shell, between the shell and the protective layer. Advantageously, the insulating layer, like the shell, is protected by the protective layer. The protective layer may thus contribute to maintaining the insulating layer in position. The properties of the insulating layer (type of insulating material, thickness of the insulating layer, form of the insulating material, etc.) are therefore not guided by the need to withstand the stresses imposed in the chamber.

[0039] It is particularly advantageous for the chamber to comprise a protective layer and an insulating layer, these two layers contributing to confer high efficiency and long service life to the regenerator.

[0040] Preferably, the insulating layer extends between the shell and the protective layer, the thermal resistance of the insulating layer, R_I, being higher than 0.1 $m^2 \cdot K/W$, preferably higher than 0.2 $m^2 \cdot K/W$, preferably higher than 0.3 $m^2 \cdot K/W$, preferably higher than 0.4 $m^2 \cdot K/W$, or even higher than 1 $m^2 \cdot K/W$, or even higher than 1.5 $m^2 \cdot K/W$, or even higher than 2 $m^2 \cdot K/W$, or even higher than 2.2 $m^2 \cdot K/W$.

[0041] The insulating layer comprises, or even consists of, a material called insulating material. Preferably:

- **[0042]** the thermal conductivity of the insulating material is lower than 2 W/m·K, preferably lower than 1.5 W/m·K, and/or
- **[0043]** the mechanical compressive strength of the insulating layer is higher than 1 MPa, preferably higher than 2 MPa, preferably higher than 5 MPa, and/or
- **[0044]** the linear thermal expansion coefficient of the insulating material, measured at 500° C., is lower than 0.5%, preferably lower than 0.4%.

[0045] Preferably, the minimum thickness of the insulating layer is higher than 150 mm, preferably higher than 300 mm.

[0046] Even more preferably,

- **[0047]** the silica content of the insulating material is lower than 50%, preferably lower than 10%, preferably lower than 1%, and/or
- **[0048]** the CaO content of the insulating material is lower than 10%, preferably lower than 5%, preferably lower than 2%, and/or
- **[0049]** the alumina content of the insulating material is higher than 40%, preferably higher than 60%, preferably higher than 80%.

[0050] Preferably, the insulating material comprises a majority compound selected from the group consisting of corundum, spinel $MgAl_2O_4$, calcined clays, mullite, hibonite $CaAl_{12}O_{19}$, aluminum titanate, bauxite, and combinations thereof.

[0051] It is also particularly advantageous to have an intermediate layer between the protective layer and the insulating layer to facilitate the sliding and to accommodate the differences in thermal expansion between the protective and insulating layers.

[0052] Preferably, the maximum thickness of the intermediate layer is lower than 10 mm and preferably comprises, or even consists of, a fibrous material.

[0053] Preferably, the intermediate layer comprises an alumina content higher than 30%, preferably higher than 70%, preferably higher than 90%.

[0054] Preferably, the intermediate layer has a thermal resistance R_{PI} higher than 0.05 $m^2 \cdot K/W$, preferably higher than 0.1 $m^2 \cdot K/W$.

[0055] The weight of the bed may be higher than 700 tonnes.

[0056] The invention also relates to a thermal installation comprising:

- **[0057]** a unit producing heat energy, for example a furnace, a solar tower, a compressor, and
- **[0058]** a regenerator according to the invention, and
- **[0059]** a circulating device which, during a charge phase, circulates a charge heat transfer fluid from the unit producing heat energy to the regenerator, and then through said regenerator.

[0060] In an embodiment, heat transfer fluid from said unit producing heat energy condenses in said regenerator in the form of an acidic liquid and/or enters the regenerator at a temperature lower than 1000° C. and higher than 350° C., or even lower than 800° C. and higher than 500° C.

[0061] A regenerator according to the invention is particularly suitable under these conditions.

[0062] The unit producing heat energy may comprise a compressor.

[0063] In an embodiment, the thermal installation further comprises a heat energy consumption unit, the circulating device circulating, during a discharge phase, a discharge heat transfer fluid through said regenerator, and then from said regenerator to the heat energy consumption unit. The heat energy consumption unit may comprise a turbine.

[0064] The invention also relates to a method for operating a thermal installation according to the invention, the insulating layer of the regenerator being adapted so that the heat losses from the regenerator, under the operating conditions, at the end of a charge and discharge cycle, are lower than 10%, that is to say, that the energy restored at the end of the discharge phase is higher than 90% of the total energy injected into the regenerator at the end of the charge phase. Preferably, these losses are lower than 8%, preferably lower than 5%, preferably lower than 3%, preferably lower than 1%, preferably, the storage time being shorter than 48 hours, preferably shorter than 24 hours.

BRIEF DESCRIPTION OF THE FIGURES

[0065] Other objects, aspects, properties and advantages of the present invention will further appear in light of the description and the examples that follow and the examination of the appended drawing in which:

[0066] FIGS. **1***a* and **1***b* schematically show a thermal installation according to the invention during a charge phase and a discharge phase, respectively;

[0067] FIG. **2** schematically shows the regenerator of the thermal installation in FIG. **1**;

[0068] FIG. **3** shows a perspective view of a portion of the side wall of the regenerator in FIG. **2**.

[0069] In the various figures, identical references are used to denote identical or similar components.

DEFINITIONS

[0070] "Unit producing heat energy" means not only units which are specifically intended to generate heat energy, like a solar tower, but also units which generate heat energy when operated, for example a compressor.

[0071] The term "thermal installation" should also be understood in the broad sense, as meaning any installation comprising a unit producing heat energy.

[0072] The term "heat energy consumption unit" designates an element capable of receiving heat energy. It may in particular cause an increase in the temperature of the consumption unit (for example in the case of heating a building) and/or a conversion to mechanical energy (for example in a gas turbine).

[0073] In the present description, for the sake of clarity, the terms "charge heat transfer fluid" and "discharge heat transfer fluid" mean the heat transfer fluid flowing in the regenerator during a charge phase and during a discharge phase, respectively.

[0074] "Bed" of energy storage media means a set of such media at least partly superimposed upon one another.

[0075] "Preform" conventionally means a set of particles joined by a binder, generally temporary, and whose microstructure evolves during sintering.

[0076] "Sintering" means a heat treatment whereby the particles of a preform are processed to form a matrix binding other particles of said preform together.

[0077] For the sake of clarity, the term "red mud" means the liquid or pasty by-product issuing from a method for producing alumina and the corresponding dried product.

[0078] The oxide contents are related to the total contents for each of the corresponding chemical elements, expressed in the most stable oxide form, according to the usual convention in the industry.

[0079] Unless otherwise indicated, all the percentages are weight percentages, based on the oxides.

[0080] "Containing a" or "comprising a" means "comprising at least one" unless otherwise indicated.

DETAILED DESCRIPTION

Thermal Installation

[0081] A thermal installation **2** according to the invention, as shown in FIG. **1**, comprises a unit producing heat energy **4**, optionally a heat energy consumption unit **6**, a circulating device **7**, optionally a cavity not shown, and a regenerator **10**.

[0082] The unit producing heat energy **4** may be intended for producing heat energy, for example a furnace or a solar tower.

[0083] Said circulating device circulates, during a charge phase, a charge heat transfer fluid from the unit producing heat energy to the regenerator, and then through said regenerator.

[0084] In an embodiment, the unit producing heat energy comprises, or even consists of, a compressor, for example supplied mechanically or electrically by an incineration plant or an electricity generating plant, in particular a thermal power, solar energy, wind energy, hydroprower, or tidal power plant.

[0085] The compression of a gaseous fluid, preferably adiabatic, leads to the storage of energy therein by increasing its pressure and its temperature.

[0086] The energy resulting from the increase in pressure can be stored by storing the pressurized fluid. The restoration of this energy may result from an expansion, for example in a turbine.

[0087] The energy resulting from the increase in temperature can be stored in a regenerator according to the invention. The restoration of this energy then results from a heat exchange with the regenerator.

[0088] The heat energy may be a production by-product, that is to say, may not be desired as such.

[0089] Preferably, the unit producing heat energy produces more than 50 kW, or even more than 100 kW of heat energy, or even more than 300 kW, or even more than 1 MW, or even more than 5 MW. The invention is in fact particularly intended for high capacity industrial installations.

[0090] The unit producing heat energy may comprise a heat exchanger adapted for direct or indirect heat exchange with the regenerator.

[0091] Preferably, a thermal installation according to the invention comprises a heat energy consumption unit **6**, said circulating device circulating, during a discharge phase, a discharge heat transfer fluid through said regenerator, and then from said regenerator to the heat energy consumption unit.

[0092] The heat energy consumption unit **6** may be in particular a building or a set of buildings, a reservoir, a basin, a turbine coupled with a generator for generating electricity, an industrial installation consuming steam, such as, for example, a paper pulp manufacturing installation.

[0093] In the embodiment shown, the heat energy consumption unit **6** comprises a heat exchanger **6***a* adapted for heat exchange between discharge heat transfer fluid issuing from the regenerator **10** (FIG. **1***b*) and a secondary circuit **6***b* in which a secondary heat transfer fluid flows. The secondary circuit is configured for implementing a heat exchange between the heat exchanger **6***a* and, for example, a building **6***c*.

[0094] The circulating device **7** comprises a charge circuit **7***a* and a discharge circuit **7***b* through which a charge heat transfer fluid and a discharge heat transfer fluid may flow, respectively. These charge and discharge circuits serve to implement a heat exchange between the unit generating heat energy **4** and the regenerator **10** during the charge phase, and the regenerator **10** and the heat energy consumption unit **6** during the discharge phase, respectively.

[0095] The circulating device **7** conventionally comprises a set of lines, valves and pumps/blowers/extractors controlled in order to make the regenerator **10** communicate selectively:

- **[0096]** with the unit producing heat energy so that it can receive the charge heat transfer fluid leaving said unit, during a charge phase (circuit **7***a*), and
- **[0097]** with the heat energy consumption unit so that the heated discharge heat transfer fluid leaving the regenerator can transfer heat energy to said consumption unit, during a discharge phase (circuit **7***b*),

and in order to force the flow of the charge heat transfer fluid and/or the discharge heat transfer fluid through the regenerator.

[0098] The temperature of the charge heat transfer fluid entering the regenerator during a charge phase is preferably lower than 1000° C., or even lower than 800° C., and/or preferably higher than 350° C., or even higher than 500° C.

[0099] The charge and discharge heat transfer fluids may or may not be of the same type.

[0100] The charge heat transfer fluid and/or the discharge heat transfer fluid may be a gas, for example air, steam, or a heat transfer gas, or may be a liquid, for example water or a thermal oil.

[0101] In an embodiment, the energy storage media are in permanent or temporary contact with an acidic liquid having a pH lower than 6, or even lower than 5.5, or even lower than 5, or even lower than 4.5, or even lower than 4, in particular aqueous. The invention is in fact particularly advantageous under these conditions.

[0102] However, the invention is not limited to particular heat transfer fluids.

[0103] Preferably, in particular when the charge and discharge heat transfer fluids are of the same type and when the charge heat transfer fluid, for example air, has undergone a temperature increase resulting from an increase in pressure, for example to 50 bar, or even 100 bar, or even 150 bar, the thermal installation may comprise a cavity for temporarily storing the charge heat transfer fluid, issuing cooled from the regenerator. The volume of the cavity is typically higher than 20 000 m^3, or even higher than 100 000 m^3.

[0104] The cavity preferably has low permeability, or is even impervious to the charge heat transfer fluid.

[0105] The regenerator **10**, shown in greater detail in FIG. **2**, comprises a bed **11** of energy storage media **12** placed in a chamber **14**.

Bed of Energy Storage Media

[0106] Preferably, the regenerator is a sensible heat regenerator, that is to say, the material of the energy storage media and the charge and discharge temperatures are determined so that the energy storage media remain solid during the operation of the thermal installation. It is in fact in a sensible heat regenerator that the probabilities of condensation of the heat transfer fluid are the highest.

[0107] Preferably, the material of the energy storage media incorporates residues from alumina production, in particular by the Bayer process, said process being described in particular in “Les techniques de l' ingénieur”, article “métallurgie extractive de l’aluminium”, reference M2340, editions T.I., published Jan. 10, 1992 (in particular chapter 6 starting on page M2340-13 and FIG. **7** on page M2340-15).

[0108] Preferably, the energy storage media are obtained by sintering a preform resulting from the shaping of an initial feed comprising more than 10%, preferably more than 30%, preferably more than 50%, preferably more than 60%, preferably more than 70%, preferably more than 80% of red mud issuing from the implementation of a Bayer process, expressed as weight percent on the basis of dry matter of the initial feed. Said red muds may optionally be converted before use, for example during washing and/or drying steps.

[0109] Preferably, the energy storage media have the following chemical analysis, in weight percent based on the oxides and for a total of 100%:

[0110] $25\% < Fe_2O_3 < 70\%$, preferably $Fe_2O_3 < 65\%$, or even $Fe_2O_3 < 60\%$ and/or preferably $Fe_2O_3 > 30\%$, preferably $Fe_2O_3 > 35\%$, preferably $Fe_2O_3 > 40\%$, or even $Fe_2O_3 > 45\%$, or even $Fe_2O_3 > 50\%$, and

[0111] $5\% < Al_2O_3 < 30\%$, preferably $Al_2O_3 < 20\%$, and

[0112] $CaO < 20\%$, and

[0113] $TiO_2 < 25\%$, preferably $TiO_2 < 20\%$, preferably $TiO_2 < 15\%$, and

[0114] $3\% < SiO_2 < 50\%$, preferably $SiO_2 < 40\%$, preferably $SiO_2 < 30\%$, preferably $SiO_2 < 20\%$, preferably $SiO_2 < 15\%$, and

[0115] $Na_2O + K_2O < 10\%$, or even $Na_2O + K_2O < 5\%$, and

[0116] $Fe_2O_3 + Al_2O_3 + CaO + TiO_2 + SiO_2 + Na_2O + K_2O > 80\%$, preferably $Fe_2O_3 + Al_2O_3 + CaO + TiO_2 + SiO_2 + Na_2O + K_2O > 85\%$, or even $Fe_2O_3 + Al_2O_3 + CaO + TiO_2 + SiO_2 + Na_2O + K_2O > 90\%$, or even $Fe_2O_3 + Al_2O_3 + CaO + TiO_2 + SiO_2 + Na_2O + K_2O > 95\%$ and

[0117] other oxides: complement to 100%.

[0118] Preferably, the energy storage media consists of over 90%, preferably over 95%, preferably over 99% of oxides.

[0119] Preferably, the energy storage media are made from a sintered material, preferably sintered at a temperature between 1000° C. and 1500° C., preferably during a holding time at this temperature longer than 0.5 hour and preferably shorter than 12 hours, and preferably in an oxidizing atmosphere, preferably in air.

[0120] The shapes and dimensions of the energy storage media **12** are not limiting. Preferably, however, the smallest dimension of an energy storage medium is higher than 0.5 mm, or even higher than 1 mm, or even higher than 5 mm, or even higher than 1 cm and/or preferably lower than 50 cm, preferably lower than 25 cm, preferably lower than 20 cm, preferably lower than 15 cm. Preferably, the largest dimension of an energy storage medium is lower than 10 meters, preferably lower than 5 meters, preferably lower than 1 meter.

[0121] The energy storage media **12** may in particular have the shape of balls and/or granules and/or solid bricks and/or openwork bricks, and/or cruciform elements and/or double cruciform elements and/or solid elements and/or openwork elements like those described in U.S. Pat. No. 6,889,963 and/or described in U.S. Pat. No. 6,699,562.

[0122] The energy storage media are assembled in the chamber **14** in order to constitute the bed **11**.

[0123] The bed may be organized, for example by bonding the energy storage media, or may be disorganized (“bulk”). For example, the bed may have the form of a mass of crushed parts (without any particular shape, such as a mass of pebbles).

[0124] The height of the bed is preferably greater than 1 m, preferably greater than 5 m, preferably greater than 15 m, preferably greater than 25 m, or even greater than 35 m, or even greater than 50 m.

[0125] The weight of the bed is preferably higher than 700 T, preferably higher than 2000 T, preferably higher than 4000 T, preferably higher than 5000 T, preferably higher than 7000 T.

Chamber

[0126] The chamber **14** is provided with a top opening **16** and a bottom opening **18**.

[0127] In an embodiment, the opening of the regenerator through which the charge heat transfer fluid enters the regenerator during a charge phase is the one through which the heated discharge heat transfer fluid leaves the regenerator during a discharge phase. Conversely, the opening of the regenerator through which the discharge heat transfer fluid to be heated enters the regenerator during a discharge phase is the one through which the cooled charge heat transfer fluid leaves the regenerator during a charge phase.

[0128] Preferably, the opening of the regenerator through which the discharge heat transfer fluid to be heated enters the regenerator is the bottom opening **18** of the regenerator.

[0129] Preferably, the opening of the regenerator through which the heated discharge heat transfer fluid leaves the regenerator is the top opening **16** of the regenerator.

[0130] The chamber **14** conventionally comprises a shell **20**, conventionally metallic, for example made of stainless steel, or a carbon steel. The shell may also consist of the wall of a natural or artificially excavated cavity, optionally provided with an inner lining for strengthening said wall and/or for leveling the surface in contact with the energy storage media. The wall of the natural cavity may in particular be rock. Preferably, the chamber **14** comprises a metal shell.

[0131] A cooling system, not shown, may be provided outside the shell, particularly if the regenerator is buried. This system may for example circulate air or a liquid, in particular water.

[0132] The shell **20** is protected internally by a protective layer **22** according to the invention, in contact with the energy storage media.

Protective Layer

[0133] The composition of the material of the protective layer, or protective material, is such that:

[0134] Preferably $Fe_2O_3+Al_2O_3+CaO+TiO_2+SiO_2+Na_2O+K_2O>85\%$, or even $Fe_2O_3+Al_2O_3+CaO+TiO_2+SiO_2+Na_2O+K_2O>90\%$;

[0135] Preferably $Fe_2O_3+Al_2O_3+SiO_2>50\%$, preferably $Fe_2O_3+Al_2O_3+SiO_2>60\%$, or even $Fe_2O_3+Al_2O_3+SiO_2>70\%$, or even $Fe_2O_3+Al_2O_3+SiO_2>80\%$, $Fe_2O_3+Al_2O_3+SIO_2>90\%$, $Fe_2O_3+Al_2O_3+SiO_2>95\%$;

[0136] Preferably, MgO, P_2O_5, and mixtures thereof account for over 90%, over 95%, or even substantially 100% of the other oxides.

[0137] In a first preferred embodiment:

[0138] $Al_2O_3>60\%$, preferably $Al_2O_3>70\%$, preferably $Al_2O_3>80\%$, preferably $Al_2O_3>85\%$, preferably $Al_2O_3>90\%$, or even $Al_2O_3>95\%$, or even $Al_2O_3>98\%$, or even $Al_2O_3>99\%$.

[0139] Advantageously, the resistance to attack by aggressive chemical agents that may be contained in a heat transfer fluid, as well as the dimensional stability, are thereby improved;

[0140] $Fe_2O_3<20\%$, preferably $Fe_2O_3<15\%$, preferably $Fe_2O_3<10\%$, preferably $Fe_2O_3<5\%$, preferably $Fe_2O_3<3\%$, preferably $Fe_2O_3<1\%$;

[0141] $SiO_2<10\%$, preferably $SiO_2<8\%$, preferably $SiO_2<7\%$, preferably $SiO_2<5\%$, or even $SiO_2<4\%$, or even $SiO_2<3\%$, or even $SiO_2<2\%$. Advantageously, the degradation by any steam that may be contained in the heat transfer fluid is thereby decreased;

[0142] $CaO<2\%$, preferably $CaO<1\%$, preferably $CaO<0.5\%$. Advantageously, the degradation due to the carbonation caused by a reaction of CaO with CO_2 that may be contained in a heat transfer fluid, is thereby decreased;

[0143] The protective material does not have a bond based on cement containing CaO;

[0144] $Na_2O+K_2O<0.5\%$, preferably $Na_2O+K_2O<0.3\%$, preferably $Na_2O+K_2O<0.2\%$.

[0145] Advantageously, the degradation of the protective material due to the formation of products subject to swelling, in particular by the presence of steam in a heat transfer fluid, is thereby decreased.

[0146] In a second embodiment, the protective material may have one or more of the following optional features:

[0147] Said protective material has a composition, in weight percent based on the oxides and for a total of 100%, such that:

[0148] $25\%<Fe_2O_3<70\%$, and

[0149] $5\%<Al_2O_3<30\%$, and

[0150] $CaO<20\%$, and

[0151] $TiO_2<25\%$, and

[0152] $3\%<SiO_2<50\%$, and

[0153] $Na_2O+K_2O<10\%$, and

[0154] other oxides<5%.

[0155] Said protective material has a Fe_2O_3 content preferably higher than 30%, preferably higher than 35%, preferably higher than 40%, or even higher than 45%, or even higher than 50%, or even higher than 60%, and/or preferably lower than 65%.

[0156] $Fe_2O_3+Al_2O_3>40\%$, preferably $Fe_2O_3+Al_2O_3>50\%$, or even $Fe_2O_3+Al_2O_3>60\%$, or even $Fe_2O_3+Al_2O_3>70\%$;

[0157] Said protective material has an Al_2O_3 content preferably lower than 25%, preferably lower than 20%;

[0158] Said protective material has a CaO content preferably higher than 3%, or even higher than 5%, or even higher than 10%;

[0159] Said protective material has a TiO_2 content preferably higher than 5%, or even higher than 10%, and/or preferably lower than 20%, preferably lower than 15%;

[0160] Said protective material has a SiO_2 content preferably higher than 5%, or even higher than 8%, and/or lower than 40%, preferably lower than 30%, preferably lower than 20%, preferably lower than 15%;

[0161] Said protective material has a Na_2O+K_2O content preferably lower than 5%;

[0162] Said protective material has an "other oxides" content preferably lower than 3%, or even lower than 2%, expressed as weight percent based on the oxides;

[0163] Preferably, the protective material consists of over 90%, preferably over 95%, preferably over 99%, or even substantially 100% of oxides, by weight percent.

[0164] Preferably, the majority compound of the protective material is selected from the group consisting of alumina, in particular corundum, bauxite, spinel $MgAl_2O_4$, mullite, hibonite $CaAl_{12}O_{19}$, aluminum titanate, and combinations thereof, preferably corundum, bauxite and spinel $MgAl_2O_4$.

[0165] The protective material preferably has an open porosity lower than 20%, preferably lower than 18%, preferably lower than 15%, preferably lower than 12%, preferably lower than 10%, preferably lower than 8%, preferably lower than 6%, preferably lower than 5%, or even lower than 4%, or even lower than 3%.

[0166] The protective material preferably has a compressive strength higher than 50 MPa, preferably higher than 60 MPa, preferably higher than 70 MPa, or even higher than 90 MPa. Advantageously, the resistance to puncture by the energy storage media, in particular when they are placed in bulk, is thereby improved, and in consequence, the mechanical deterioration of the protective layer is reduced and the service life of the regenerator is increased.

[0167] The protective material preferably has a pyroscopic resistance higher than the temperature of the heat transfer fluid entering the regenerator during the charge. Preferably, the protective material has a pyroscopic resistance higher than 350° C., higher than 500° C., higher than 700° C., higher than 800° C., higher than 900° C., higher than 1000° C.

[0168] A person skilled in the art knows how to modify the open porosity, the compressive strength and the pyroscopic resistance.

[0169] The minimum thickness, preferably the average thickness, of the protective layer is preferably higher than 75 mm, preferably higher than 100 mm, preferably higher than 150 mm, preferably higher than 180 mm, and/or preferably lower than 500 mm, preferably lower than 400 mm, preferably lower than 300 mm, preferably lower than 250 mm.

[0170] The thickness of the protective layer and the type of protective material are preferably adapted so that, in particular when the heat transfer fluid is air and/or water vapor, the condensation isotherm is located in the thickness of the protective layer. Advantageously, the penetration of water is thereby delayed and the service life of the regenerator is thereby increased.

[0171] The protective material may be a molten, poured or sintered product. The protective material may in particular be a concrete, preferably self-placing, a mud brick, dry or wet. Preferably, the protective material is a concrete.

[0172] The shaping of the protective material may result from a pouring, in particular a vibratory pouring, a pressing, in particular a vibratory pressing or an isostatic pressing, a ramming, an extrusion, or a combination of these well known techniques. Preferably, the shaping of the protective material results from a vibratory pouring or a pressing.

[0173] The protective layer preferably consists of an array of shaped parts or "blocks", the shape of these blocks not being limiting, as shown in FIG. **3**.

[0174] For example, the protective layer may have the form of an assembly of ring-shaped blocks superimposed upon one another.

[0175] Preferably, the bricks have complementary shapes to enable their nesting, as shown in FIG. **3**, for example with grooved or flanged edges.

[0176] Preferably, the blocks are jointed, preferably with a jointing material such as a grout, a mortar or a mud, the jointing techniques being known to a person skilled in the art.

[0177] Preferably, the alumina content of the jointing material is higher than 80%, preferably higher than 85%, preferably higher than 90%, or even higher than 95%, in weight percent based on the oxides.

[0178] The protective layer may also be in a single piece, in particular if the regenerator is small.

[0179] It may result from a shaping, in particular a pouring, in situ (in the regenerator) or not (the protective layer or its components (blocks) being shaped before assembly in the regenerator). Preferably, it is shaped in situ.

[0180] Preferably, the protective layer contains less than 10% water, preferably less than 7%, preferably less than 5%, or even less than 3%, or even less than 2%, or even less than 1%. Advantageously, the temperature buildup of the regenerator is thereby accelerated.

[0181] In an embodiment, holes **23** run through the protective layer, preferably in the direction of its thickness. These holes may in particular be made through the joints or through the blocks. These holes, for example drilled, may for example have an equivalent diameter of between 3 and 10 mm, for example 5 mm. Preferably, they are uniformly distributed, for example at the rate of one hole in each block, for example at the center of each block, or according to a predefined mesh, for example a square mesh with 1 m sides.

[0182] Advantageously, these holes serve to balance the pressures on either side of the protective layer. The service life of the protective layer is thereby increased.

[0183] In another embodiment, the protective layer forms an impervious barrier between the shell and the energy storage media.

[0184] Preferably, an insulating layer **24** extends between the shell **20** and the protective layer **22**.

[0185] The thermal resistance of the insulating layer, R_I, is preferably higher than 0.1 $m^2 \cdot K/W$, preferably higher than 0.2 $m^2 \cdot K/W$, preferably higher than 0.3 $m^2 \cdot K/W$, preferably higher than 0.4 $m^2 \cdot K/W$, or even higher than 1 $m^2 \cdot K/W$, or even higher than 1.5 $m^2 \cdot K/W$, or even higher than 2 $m^2 \cdot K/W$, or even higher than 2.2 $m^2 \cdot K/W$.

[0186] The thermal conductivity of the material of the insulating layer, called "insulating material", is preferably more than 20%, preferably more than 50%, lower than that of the protective material, or even more than 70% lower than that of the protective material. Preferably, it is lower than 2 W/m·K, preferably lower than 1.5 W/m·K, preferably lower than 1 W/m·K. In a particular embodiment, the thermal conductivity of the insulating material is between 1 W/m·K and 1.5 W/m·K.

[0187] The minimum thickness, or even the average thickness, of the insulating layer is preferably higher than 150 mm, preferably higher than 200 mm, preferably higher than 300 mm, preferably higher than 400 mm, and/or lower than 600 mm.

[0188] In a particular embodiment, the thermal conductivity of the insulating material is between 1 W/m·K and 1.5 W/m·K, and the average thickness of the insulating layer is higher than 150 mm, preferably higher than 200 mm.

[0189] In a particular embodiment, the thermal conductivity of the insulating material is between 1.5 W/m·K and 2 W/m·K, and the average thickness of the insulating layer is higher than 300 mm, preferably higher than 400 mm.

[0190] Preferably, the mechanical compressive strength of the insulating material is higher than 1 MPa, preferably higher than 2 MPa, or even higher than 3 MPa, or even higher than 5 MPa. Advantageously, the mechanical strength of the insulating layer thereby contributes to the mechanical strength of the regenerator wall.

[0191] The linear thermal expansion coefficient of the insulating material, measured at 500° C., is preferably lower than $15 \cdot 10^{-6\circ} C.^{-1}$, preferably lower than $10 \cdot 10^{-6\circ} C.^{-1}$, or even lower than $8 \cdot 10^{-6\circ} C.^{-1}$.

[0192] A person skilled in the art knows how to modify the thermal conductivity, mechanical compressive strength and linear thermal expansion coefficient of the insulating material.

[0193] The insulating material preferably consists of over 90% oxides, preferably over 95%, preferably over 99%, preferably substantially 100% of its mass.

[0194] Preferably, the insulating material is a ceramic material. Preferably, the insulating material has a chemical composition such that $Fe_2O_3+Al_2O_3+SiO_2+ZrO_2>60\%$, preferably $Fe_2O_3+Al_2O_3+SiO_2+ZrO_2>70\%$, preferably $Fe_2O_3+Al_2O_3+SiO_2+ZrO_2>80\%$, preferably $Fe_2O_3+Al_2O_3+SiO_2+ZrO_2>90\%$, in weight percent based on the oxides. Preferably, the complement to 100% consists of oxides, preferably selected from TiO_2, CaO, MgO, K_2O, Na_2O, P_2O_5, and mixtures thereof.

[0195] Preferably, the silica content of the insulating material is lower than 50%, or even lower than 40%, or even lower than 30%, or even lower than 10%, or even lower than 1%, in weight percent based on the oxides. Advantageously, corrosion by aggressive chemical agents liable to condense in the thickness of the insulating layer, for example caustic soda, is thereby decreased.

[0196] Preferably, the CaO content of the insulating material is lower than 10%, preferably lower than 5%, preferably lower than 2%, preferably lower than 1%, in weight percent based on the oxides. Advantageously, the carbonation sensitivity of the insulating material is thereby decreased, and the service life of the regenerator is thereby increased.

[0197] Preferably, the alumina content of the insulating material is higher than 40%, preferably higher than 50%, preferably higher than 60%, preferably higher than 65%, preferably higher than 70%, or even higher than 80%, or even higher than 90%, in weight percent based on the oxides.

[0198] Preferably, the majority compound of the insulating material (component having the highest weight content) is selected from the group consisting of corundum, spinel $MgAl_2O_4$, calcined clays, mullite, hibonite $CaAl_{12}O_{19}$, aluminum titanate, bauxite, and combinations thereof.

[0199] The insulating material may be molten, poured or sintered material. The insulating material may in particular be a concrete, preferably self-placing, a mud block, dry or wet. Preferably, the insulating material is a concrete. Preferably, the insulating material is a dry mud block installed by ramming or a concrete, preferably self-placing.

[0200] The shaping of the insulating material may result from a pouring, in particular from a vibratory pouring, a pressing, in particular a vibratory pressing, or an isostatic pressing, a ramming, an extrusion or a combination of these well known techniques. Preferably, the shaping of the insulating material results from a pouring with vibration or a pressing.

[0201] The insulating layer preferably consists of an array of shaped parts, or "blocks", the shape of these blocks not being limiting. Preferably, the blocks are jointed, preferably with a jointing material such as a grout, a mortar or a mud. Preferably, the joints of the blocks of the insulating layer are offset with regard to those of the protective layer. The protection of the shell is thereby improved.

[0202] The insulating layer may also be in a single piece, in particular if the regenerator is small.

[0203] It may result from a shaping, in particular a pouring, in situ (in the regenerator) or not (the insulating layer or its components (blocks) being shaped before assembly in the regenerator). Preferably, it is shaped in situ.

[0204] Preferably, the insulating layer contains less than 10% water, preferably less than 7%, preferably less than 5%, or even less than 3%, or even less than 2%, or less than 1%. Advantageously, the temperature buildup of the regenerator is thereby accelerated.

[0205] Preferably, an intermediate layer **26** extends between the protective layer **22** and the insulating layer **24**. The intermediate layer is intended to facilitate the sliding and to accommodate the differences in thermal expansion between the protective and insulating layers, in particular during charge and discharge cycles.

[0206] Preferably, it extends parallel to the outer face of the protective layer, preferably in contact with said outer face, as shown in FIG. **3**.

[0207] The intermediate layer may comprise, or even consist of, a fibrous material, in particular cardboard and/or a mixture of interlaced fibers, preferably a mixture of fibers. The fiber mixture is preferably in the form of boards and/or sheets, woven or nonwoven. Preferably, the fibers are ceramic fibers.

[0208] The maximum thickness of the intermediate layer is preferably lower than 10 mm, preferably lower than 8 mm, preferably lower than 6 mm, preferably lower than 5 mm.

[0209] In an embodiment, the intermediate layer comprises an alumina content higher than 30%, preferably higher than 50%, preferably higher than 70%, preferably higher than 80%, preferably higher than 90%, preferably higher than 95%, preferably higher than 99%.

[0210] Preferably, the intermediate layer has a thermal resistance R_{PI} higher than 0.05 $m^2 \cdot K/W$, preferably higher than 0.1 $m^2 \cdot K/W$.

[0211] In a preferred embodiment, the insulating layer is prepared in situ, after having placed the protective layer, by filling the space remaining between said protective layer and the shell.

[0212] Preferably, an intermediate layer is placed in this space, preferably in contact with the protective layer, before said filling.

[0213] The wall of the chamber consists of an upper wall **30**, a lower wall **32** and a side wall **34**. The protective layer, preferably the insulating layer and preferably the intermediate layer, extend at least into the side wall **34**, preferably at least into the entire portion of the side wall **34** facing the bed of energy storage media. They may also extend into the lower wall **32** and/or into the upper wall **30**.

[0214] In a particular embodiment, the regenerator comprises

- **[0215]** a protective layer having:
  - **[0216]** an open porosity lower than 20%, preferably lower than 18%, preferably lower than 15%, preferably lower than 12%, preferably lower than 10%, preferably lower than 8%, preferably lower than 6%, preferably lower than 5%, or even preferably lower than 4%, or even preferably lower than 3%, and
  - **[0217]** a compressive strength higher than 50 MPa, preferably higher than 60 MPa, preferably higher than 70 MPa, and even higher than 90 MPa, and
  - **[0218]** a pyroscopic resistance higher than 350° C., preferably higher than 700° C., preferably higher than 900° C., and
  - **[0219]** a thermal resistance R_P of between 0.01 and 0.05 $m^2 \cdot K/W$, and
- **[0220]** an insulating layer having:
  - **[0221]** a compressive strength higher than 1 MPa, preferably higher than 2 MPa, or even 3 MPa, or even 5 MPa, and
  - **[0222]** made from an insulating material having a thermal resistance R_I higher than 0.20 $m^2 \cdot K/W$, preferably higher than 0.43 $m^2 \cdot K/W$, or even higher than 2.21 $m^2 \cdot K/W$.

[0223] The heat losses of such a regenerator at the end of a charge and discharge cycle are lower than 10% if $R_{(B)}$ is higher than 0.20 $m^2 \cdot K/W$, lower than 5% if $R_{(B)}$ is higher than 0.43 $m^2 \cdot K/W$, and even lower than 1% if $R_{(B)}$ is higher than 2.21 $m^2 \cdot K/W$.

Operation

[0224] The regenerator undergoes a succession of regular or irregular "cycles", each cycle comprising a charge phase, optionally a waiting phase, followed by a discharge phase. The duration of a regular cycle is generally longer than 0.5 hour, or even longer than two hours and/or shorter than 48 hours, or even shorter than 24 hours.

[0225] During a charge phase, the charge heat transfer fluid enters the regenerator at a temperature Tc, preferably substantially constant, and generally via the top opening **16** of the regenerator. Preferably, the temperature Tc at which the charge heat transfer fluid enters the regenerator during its charge is lower than 1000° C., or even lower than 800° C., and/or preferably higher than 350° C., or even higher than 500° C.

[0226] The charge heat transfer fluid then continues its route in the regenerator (arrows in FIG. **1***a*), while heating the energy storage media with which it is in contact. Its temperature therefore drops progressively.

[0227] When the charge heat transfer fluid is a gas, its cooling may lead to condensation on the surface of the energy storage media, in particular in sensible heat regenerators.

[0228] At high temperature, like those considered above in particular, the condensates may be highly corrosive.

[0229] During a discharge phase, the discharge heat transfer fluid enters the regenerator at a temperature Td, preferably substantially constant, in general via the top opening **18** of the regenerator. The heat transfer fluid then continues its route in the regenerator (arrows in FIG. **1***b*), while cooling the energy storage media with which it is in contact. Its temperature therefore progressively increases.

[0230] In an embodiment, the insulating layer of the regenerator is adapted so that the heat losses of the regenerator, in the operating conditions, at the end of a charge and discharge cycle, are lower than 10%, preferably lower than 8%, preferably lower than 5%, or even lower than 3%, or even lower than 1%.

EXAMPLES

[0231] The following examples are provided for illustrative purposes and are nonlimiting.

[0232] The apparent density and open porosity are determined according to standard ISO5017, after drying for example 2.

[0233] The chemical analysis is carried out by X-ray fluorescence.

[0234] The compressive strength is determined according to standard EN993-5.

[0235] The pyroscopic resistance is determined by the following methods: ISO 1893 (collapse under load).

[0236] The thermal expansion coefficient is determined by the following method: EN993-19.

[0237] The thermal conductivity of the material of the protective layer and of the material of the insulating layer is determined by the following method: ISO8894-2.

[0238] The thermal conductivity of the material of the intermediate layer in the form of a fiber felt is measured according to the following standard: ASTM C-177.

[0239] The following assumptions were used to calculate the heat losses:

[0240] square regenerator, with constant cross-section, sides having a length of 4.43 m and a height of 20 m;

[0241] charge and discharge heat transfer fluids: dry air;

[0242] type and volume of energy storage media constant;

[0243] total quantity of energy stored 3.77 10^{11} J;

[0244] duration of a compete cycle: 22 hours, with a total duration of the charge phase of 4 hours, a storage time of 10 hours and a total duration of the discharge phase of 8 hours;

[0245] Tc: average temperature in the regenerator at the end of the charge phase equal to 550° C.;

[0246] Td: average temperature in the regenerator at the end of the discharge phase equal to 150° C.;

[0247] cooling of the outer shell by water, at a temperature of 50° C. and with a heat exchange coefficient of 100 W/m^{2}K.

[0248] The following formula gives an evaluation of the heat losses across the regenerator walls, after a complete cycle, that is to say, a charge phase and a discharge phase:

$$\int_0^{t_{cycle}} \frac{T_{int}(t) - T_{ext}}{R_P + R_I + R_{PI} + R_h} \cdot S_{int} \cdot dt$$

[0249] In this formula:

[0250] T_{int} (t): average internal temperature of the regenerator, in kelvins;

[0251] T_{ext}: external temperature of the regenerator, constant, in kelvins;

[0252] S_{int}: internal area of the regenerator, in m^2;

[0253] t_{cycle}: duration of a complete cycle in seconds;

[0254] R_P: thermal resistance of the protective layer, in m^2·K/W, equal here to the thickness of the protective layer divided by the thermal conductivity of the material of said layer;

[0255] R_I: thermal resistance of the insulating layer, m^2·K/W, here equal to the thickness of the insulating layer divided by the thermal conductivity of the material of said layer;

[0256] R_{PI}: thermal resistance of the intermediate layer, in m^2·K/W, here equal to the thickness of the intermediate layer divided by the thermal conductivity of the material of said layer;

[0257] R_h: heat exchange resistance between the shell and the water of the cooling system, in m^2·K/W, here equal to the inverse of the heat exchange coefficient at the outer surface of the regenerator.

[0258] The following formula gives an evaluation of the total energy injected into the regenerator, equal to the sum of the energy stored at the end of the charge phase and the heat losses occurring during said phase:

$$\begin{aligned} E_{injected} &= E_{stored} + E_{losses}^{charge} \\ &= M \cdot Cp \cdot (Tc - Td) + \int_0^{t_{charge}} \frac{T_{int}(t) - T_{ext}}{R_P + R_I + R_{PI} + R_h} \cdot S_{int} \cdot dt \end{aligned}$$

[0259] In this formula:

[0260] M: total weight of energy storage media, equal to 785000 kg;

[0261] Cp: heat capacity of energy storage media, equal to 1200 J/kg·K;

[0262] t_{charge}: duration of the charge phase, equal to 14400 s.

[0263] Comparative example 1 is a regenerator whereof the side wall comprises an insulating layer having a constant thickness of 420 mm, consisting of insulating bricks R130 containing 70% Al_2O_3, sold by Distrisol.

[0264] Example 2, according to the invention, is a regenerator whereof the side wall is formed as follows:

[0265] The protective layer has a thickness of 200 mm and consists of Monoguard® aluminous concrete, sold by Savoie Refractaires. It results from an assembly of blocks measuring

1000×1000×200 mm^3, shaped by a vibratory pouring technique and dried at 400° C. before placement in the regenerator. These blocks were jointed with cement **337** (cement containing 86% Al_2O_3, sold by Savoie Refractaires).

[0266] The outer face of the protective layer is covered with an intermediate layer of Insulfrax Paper fiber felt, thickness 6 mm, sold by Unifrax.

[0267] The insulating layer has a thickness of 500 mm and consists of a Y75LCC self-placing concrete, sold by Savoie Refractaires, and placed by pouring between the regenerator shell and the protective layer, which thus act as a formwork.

[0268] Example 3, according to the invention, is a regenerator whereof the side wall is identical to that of the regenerator in example 2, without the intermediate layer of Insulfrax Paper fiber felt.

[0269] Example 4, according to the invention, is a regenerator whereof the side wall is formed as follows:

[0270] The protective layer is identical to that of example 2, but has a thickness of 300 mm.

[0271] The insulating layer has a thickness of 500 mm and consists of a VK130 dry refractory mix, sold by Saint Gobain Industrie Keramik, and placed by ramming between the regenerator shell and the protective layer.

[0272] Example 5, according to the invention, is a regenerator whereof the side wall is formed as follows:

[0273] The protective layer is identical to that of example 2, but consists of Pural T aluminous concrete containing 95% Al_2O_3.

[0274] The insulating layer has a thickness of 300 mm and consists of RI30 insulting bricks containing 70% Al_2O_3, sold by Distrisol, assembled prior to the protective layer and jointed with cement **337**.

[0275] Example 6, according to the invention, is a regenerator whereof the side wall is formed as follows:

[0276] The protective layer has a thickness of 150 mm and consists of AL100, which is a product containing over 99% Al_2O_3, sold by Savoie Refractaires. It results from an assembly of bricks having a cross-section of 400×400 mm^2, jointed with cement.

[0277] The outer face of the protective layer is covered with an intermediate layer of Zircar APA-2 fiber felt, thickness of 1.25 mm.

[0278] The insulating layer has a thickness of 600 mm and consists of a Y75LCC self-placing concrete, sold by Savoie Refractaires, placed by pouring between the regenerator shell and the bricks of the protective layer, which thus act as a formwork.

[0279] The results obtained are given in the table below.

[0280] In the table, the protective, intermediate and insulating layers are denoted by "P", "PI" and "I" respectively.

TABLE 1

		Example 2			Example 3			Example 4		
	Example 1	P	I	PI	P	I	PI	P	I	PI
Regenerator characteristics										
% Al_2O_3	70	88	44		88	44	—	88	68	—
% SiO_2	28	4	47	64	4	47	—	4	27	—
% CaO	0.2	0.2	6	30	0.2	6	—	0.2	0.4	—
% $Na_2O + K_2O$	0.2	0.1	0.2		0.1	0.2		0.1	0.3	
Thickness (mm)	300	200	500	6	200	500	—	300	500	—
Open porosity (%)	—	9	17		9	17	—	9	18	—
Compressive strength (MPa)	3	130	65		130	65	—	130	20	—
Pyroscopic resistance (° C.)	1650	1600	850	1260	1600	850	—	1600	1760	—
Thermal conductivity at 200° C. (W/m · K)	0.4	3.8	1.1	0.06	3.8	1.1		3.8	1.2	
Thermal resistance R ($m^2 \cdot K/W$)	0.75	0.053	0.45	0.1	0.053	0.45	—	0.08	0.42	—
Thermal expansion coefficient ($10^{-6} \cdot C^{-1}$)	6.5	7.5	5.5		7.5	5.5		7.5	5.5	
Quantity of total energy injected into the regenerator at the end of the charge phase (J)		3.79 10^{11}			3.80 10^{11}			3.80 10^{11}		
Heat losses in (J)		1.78 10^{10} J			2.12 10^{10} J			2.17 10^{10} J		
Heat losses in (%)		4.7%			5.6%			5.7%		

	Example 5			Example 6		
	P	I	PI	P	I	PI
Regenerator characteristics						
% Al_2O_3	95	70		99	44	86
% SiO_2	0.1	28		0.2	47	10
% CaO	4.5	0.2		0.2	6	—
% $Na_2O + K_2O$		0.2		0.2	0.2	—
Thickness (mm)	200	300		200	600	1.25
Open porosity (%)	5	—		17	17	
Compressive strength (MPa)	75	3		95	65	
Pyroscopic resistance (° C.)	1800	1650		1675	850	1650
Thermal conductivity at 200° C. (W/m · K)	2.0	0.4		3.2	1.1	0.06
Thermal resistance R ($m^2 \cdot K/W$)	0.1	0.75		0.05	0.55	0.02
Thermal expansion coefficient ($10^{-6} \cdot C^{-1}$)	8	6.5		8.3	5.5	

TABLE 1-continued

Quantity of total energy injected into the regenerator at the end of the charge phase (J)	$3.79\ 10^{11}$	$3.79\ 10^{11}$
Heat losses in (J)	$1.28\ 10^{10}$ J	$1.72\ 10^{10}$ J
Heat losses in (%)	3.4%	4.5%

[0281] Under the operating conditions described above, a regenerator according to the invention serves to minimize the thermal losses, as shown in Table 2 below:

TABLE 2

	R_I in absence of intermediate layer			R_I in presence of an intermediate layer (Insulfrax Paper thickness 6 mm)		
R_P	Losses <10%	Losses <5%	Losses <1%	Losses <10%	Losses <5%	Losses <1%
$0.01 \leq R_P \leq 0.05$	≥ 0.23	≥ 0.52	≥ 2.85	≥ 0.13	≥ 0.42	≥ 2.75
$0.05 < R_P \leq 0.1$	≥ 0.18	≥ 0.47	≥ 2.80	≥ 0.08	≥ 0.37	≥ 2.70
$0.1 < R_P \leq 0.2$	≥ 0.08	≥ 0.37	≥ 2.70		≥ 0.27	≥ 2.60
$0.2 < R_P \leq 0.3$		≥ 0.27	≥ 2.60		≥ 0.17	≥ 2.50
$0.3 < R_P \leq 0.4$		≥ 0.17	≥ 2.50		≥ 0.07	≥ 2.40
$0.4 < R_P \leq 0.5$		≥ 0.07	≥ 2.40			≥ 2.30

[0282] The present invention is of course not limited to the embodiments described and shown, provided as examples. In particular, combinations of the various embodiments described or shown also fall within the scope of the invention.

[0283] Nor is the invention limited by the shape or dimensions of the regenerator.

[0284] Finally, the energy storage media may be in contact with a neutral or basic environment.

1. A regenerator comprising a bed (**11**) of energy storage media (**12**) placed in a chamber (**14**), the chamber comprising a shell (**34**) and a protective layer (**22**) placed between said shell and said energy storage media, in contact with said energy storage media, having a minimum thickness higher than 50 mm and consisting, at least partially, of a protective material having a composition, in weight percent based on the oxides, such that:

$Fe_2O_3+Al_2O_3+CaO+TiO_2+SiO_2+Na_2O+K_2O>80\%$, and
other oxides: complement to 100%.

2. The regenerator as claimed in claim **1**, in which the composition of the material of the protective layer, or protective material is such that:

$Fe_2O_3+Al_2O_3+SiO_2>80\%$ and
$Al_2O_3>60\%$, and
$Fe_2O_3<20\%$, and/or
$SiO_2<10\%$, and/or
$CaO<2\%$, and/or
$Na_2O+K_2O<0.5\%$.

3. (canceled)

4. (canceled)

5. (canceled)

6. (canceled)

7. (canceled)

8. (canceled)

9. (canceled)

10. The regenerator as claimed in claim **1**, in which the protective material has a composition, in weight percent based on the oxides and for a total of 100%, such that:

$25\%<Fe_2O_3<70\%$, and
$5\%<Al_2O_3<30\%$, and
$CaO<20\%$, and
$TiO_2<25\%$, and
$3\%<SiO_2<50\%$, and
$Na_2O+K_2O<10\%$, and
other oxides<5%.

11. (canceled)

12. The regenerator as claimed in claim **1**, in which the protective material comprises a majority compound selected from the group consisting of alumina, bauxite, spinel $MgAl_2O_4$, mullite, hibonite $CaAl_{12}O_{19}$, aluminum titanate, and combinations thereof.

13. The regenerator as claimed in claim **1**, in which the protective material has:

an open porosity lower than 20%, and
a compressive strength higher than 50 MPa, and
a pyroscopic resistance higher than 350° C.

14. (canceled)

15. (canceled)

16. The regenerator as claimed in claim **1**, in which the minimum thickness of the protective layer is higher than 100 mm.

17. (canceled)

18. The regenerator as claimed in claim **1**, in which the protective layer is run through by holes (**23**).

19. The regenerator as claimed in claim **1**, in which the protective layer is a single piece.

20. The regenerator as claimed in claim **1**, comprising an insulating layer (**24**) extending between the shell (**20**) and the protective layer (**22**), the thermal resistance of the insulating layer being higher than 0.1 $m^2\cdot K/W$.

21. (canceled)

22. The regenerator as claimed in claim **20**, in which the insulating layer comprises an insulating material, and in which:

the thermal conductivity of the insulating material is lower than 2 $W/m\cdot K$, and/or the mechanical compressive strength of the insulating layer is higher than 1 MPa, and/or

the linear thermal expansion coefficient of the insulating material, measured at 500° C., is lower than 0.5%, and/or

in which the minimum thickness of the insulating layer is higher than 150 mm, and/or in which:

the silica content of the insulating material is lower than 50%, and/or

the CaO content of the insulating material is lower than 10%, and/or

the alumina content of the insulating material is higher than 40%.

23. (canceled)

24. (canceled)

25. (canceled)

26. (canceled)

27. (canceled)

28. (canceled)

29. (canceled)

30. (canceled)

31. The regenerator as claimed in claim **20**, comprising an intermediate layer (**26**) extending between the protective layer (**22**) and the insulating layer (**24**), the maximum thickness of the intermediate layer being lower than 10 mm and the intermediate layer comprising a fibrous material.

32. The regenerator as claimed in claim **31**, in which the intermediate layer comprises an alumina content higher than 30% and/or has a thermal resistance R_{PI} higher than 0.05 $m^2 \cdot K/W$.

33. (canceled)

34. (canceled)

35. (canceled)

36. The regenerator as claimed in claim **32**, in which the weight of the bed is higher than 700 tonnes.

37. A thermal installation comprising:

a unit producing heat energy (**4**), and

a regenerator (**10**) as claimed in claim **1**, and

a circulating device (**7**) which, during a charge phase, circulates a charge heat transfer fluid from the unit producing heat energy to the regenerator, and then through said regenerator.

38. A method for operating a thermal installation as claimed in the claim **37**, in which heat transfer fluid from said unit producing heat energy (**4**) condenses in said regenerator (**10**) in the form of an acidic liquid.

39. The method for operating a thermal installation as claimed in claim **37**, in which the temperature of the heat transfer fluid from said unit producing heat energy (**4**) and entering the regenerator is lower than 1000° C. and higher than 350° C.

40. (canceled)

41. The method for operating a thermal installation as claimed in claim **37**, in which the unit producing heat energy comprises a compressor.

42. The method for operating a thermal installation as claimed in claim **37**, said installation comprising a heat energy consumption unit (**6**), the circulating device (**7**) circulating, during a discharge phase, a discharge heat transfer fluid through said regenerator, and then from said regenerator to the heat energy consumption unit.

43. The method for operating a thermal installation as claimed in claim **42**, in which the heat energy consumption unit comprises a turbine.

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