(54) Title: REGENERATOR WITH COMPOSITE INSULATING WALL

(57) Abstract: The present invention relates to a regenerator comprising a bed of energy storage media placed in a chamber, the chamber comprising a shell and an insulating layer placed between said shell and said energy storage media, the insulating layer comprising a structure defining a plurality of cavities, each cavity having a volume greater than 5 cm³, at least a portion of said cavities being filled, at least partly, with an insulating material, the minimum thickness of the structural material separating the cavities and the internal volume of the chamber wherein the energy storage media are placed being higher than 2 mm.
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Regenerator with composite insulating wall

Technical field

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

Technical background

The storage of energy, for example heat energy, serves to create a time offset between the production and the consumption of said energy.

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.

The heat energy is conventionally stored in a packed bed of energy storage media, for example a pebble bed, placed in a chamber of a regenerator. This chamber may comprise a shell that is internally insulated by an insulating layer in order to improve the energy efficiency.

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".

Conventionally, the charge heat transfer fluid enters the regenerator at a temperature, preferably substantially constant, higher than 350°C, or even higher than 500°C (and generally lower than 1000°C, or even lower than 800°C).

The charge heat transfer fluid then continues its route in the regenerator, while heating the energy storage media with which it is in contact. Its temperature therefore falls progressively to a temperature typically between 20°C and 350°C. The transfer of heat energy can cause an increase in the temperature of the energy storage media ("sensible" heat storage) and/or a phase change of these media ("latent" heat storage).

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".
The regenerator thereby undergoes a succession of "cycles", regular or irregular, 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.

"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.

A permanent need exists to improve the energy efficiency of the regenerators.

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

Summary of the invention

According to the invention, this goal 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, preferably metallic, and an insulating layer placed preferably between said shell and said energy storage media or outside said shell.

The insulating layer is characterized in that it comprises a structure defining a plurality of cavities, each cavity having a volume greater than 5 cm³, at least a portion of said cavities being filled, at least partly, with an insulating material.

The inventors have discovered that such an insulating layer yields a remarkable energy efficiency. Without being bound by this theory, they explain this result by the capacity of the cavities to limit, or even prevent, gas flows, in the insulating layer. In fact, these flows, resulting from sometimes very high thermal gradients in the insulating layer of a regenerator, in particular according to the length of the regenerator, are detrimental to the thermal insulation, and hence to the energy efficiency.

Preferably, a regenerator according to the invention further comprises one, and preferably more, of the following optional features:

- The structure is made of a structural material having the following chemical analysis, in weight percent based on the oxides and for a total of 100%:
  - 25% < Fe₂O₃ < 90%, preferably Fe₂O₃ < 70%, and
  - 5% < Al₂O₃ < 30%, and
  - CaO < 20%, and
  - TiO₂ < 25%, and
  - 3% < SiO₂ < 50%, and
  - Na₂O + K₂O < 10%, and
  - other oxides < 20%
- The structure is made of a structural material having the following chemical analysis, in weight percent based on the oxides and for a total of 100%:
  - 40% < Fe₂O₃ < 60%, and/or
- \( \text{Al}_2\text{O}_3 < 20\% \), and/or
- \( 3\% < \text{CaO} \), and/or
- \( 5\% < \text{TiO}_2 < 15\% \), and/or
- \( 5\% < \text{SiO}_2 < 20\% \), and/or
- \( \text{Na}_2\text{O} < 5\% \), and/or
- other oxides < 5%.

- The structure is made of a structural material of which more than 50% of the mass consists of one or more of the following compounds: iron oxides, alumina, magnesia, zirconia, silica, preferably crystalline silica, titanium dioxide, and calcium oxide, in particular aluminum-magnesium spinel, steatite, forsterite and ilmenite (FeTiO\(_3\)).

- The structure is made of a structural material having
  - a chemical composition substantially identical to that of the material constituting the energy storage media and/or substantially identical to that of the insulating material, and/or
  - an open porosity lower than 20%, and/or
  - a compressive strength higher than 10 MPa, and/or
  - a pyroscopic resistance higher than 700°C.

- The structure consists of a bonding of structural blocks.
- The thickness of the insulating layer is formed by a plurality of structural blocks.
- The minimum thickness of the insulating layer is higher than 150 mm, preferably higher than 400 mm.
- The thermal resistance of the insulating layer is higher than 1 m\(^2\).K/W, preferably higher than 1.2 m\(^2\).K/W.
- The insulating material has a chemical composition such that \( \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{ZrO}_2 + \text{B}_2\text{O}_3 + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{K}_2\text{O} > 60\% \), preferably such that \( \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{ZrO}_2 + \text{B}_2\text{O}_3 + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{K}_2\text{O} > 90\% \).
- The compound of the insulating material having the highest weight content is selected from the group consisting of corundum, spinel \( \text{MgAl}_2\text{O}_4 \), calcined clays, mullite, hibonite, aluminum titanate, bauxite and combinations thereof.
- The insulating material has the physical structure of a foam or of a mixture of fibers.
- More than 50% by number of the cavities containing insulating material are through cavities.
- The cavities account for more than 50% of the volume defined by the structure.
- More than 50% by number of the cavities are filled at least partially, preferably completely, with insulating material.
- The ratio of the volume of the insulating material of a cavity to the volume of said cavity is higher than 50%, preferably substantially equal to 100%.
- The structural material and the insulating material are chemically substantially identical.
The structural material is chemically substantially identical to the insulating material and to the material constituting the energy storage media.

- The regenerator comprises at least first and second cavities filled with first and second insulating materials, respectively,
- the first and second cavities having different shapes and/or volumes and/or bulk densities and/or orientations and/or filling ratios with the first and second insulating materials and/or
- the first and second insulating materials having different chemical compositions and/or physical structures and/or densities.
- The cavities are arranged so that any imaginary straight line crossing the insulating layer in the direction of the thickness of said insulating layer necessarily passes through at least one cavity.
- The weight of the bed is higher than 700 tonnes.

The invention also relates to a thermal installation comprising:
- a unit producing heat energy, for example a furnace, a solar tower, a compressor, and
- a regenerator according to the invention, and
- 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.

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.

The unit producing heat energy may comprise a compressor.

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.

**Brief description of the figures**

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:
- figures 1a and 1b schematically show a thermal installation according to the invention during a charge phase and a discharge phase, respectively;
- Figure 2 schematically shows the regenerator of the thermal installation in figure 1;
- Figures 3a and 3b show a plan and perspective view of two examples of brick suitable for
  the fabrication of a regenerator according to the invention.

In figures 3a and 3b, identical references are used to denote identical or similar members. In
figure 3b, the references have however been given a "prime" sign.

Definitions

A "cavity" is a volume bounded by a wall. A cavity may be open or closed.

Unless otherwise indicated, a "filling" of a cavity with insulating material does not mean that
the cavity is completely filled with insulating material.

"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.

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

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).

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.

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

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

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

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.

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.

Unless otherwise indicated, all the percentages are weight percentages, based on the
oxides.
"Containing a" or "comprising a" means "comprising at least one" unless otherwise indicated.

**Detailed description**

**Thermal installation**

A thermal installation 2 according to the invention, as shown in figures 1a and 1b, 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.

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

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.

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, hydropower, or tidal power plant.

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

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.

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.

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

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.

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

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, then from said regenerator to the heat energy consumption unit.
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.

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

**The circulating device** 7 comprises a charge circuit 7a and a discharge circuit 7b 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 producing 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.

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

- with the unit producing heat energy so that it can receive the charge heat transfer fluid leaving said unit, during a charge phase (circuit 7a), and
- 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 7b),

and in order to force the flow of the charge heat transfer fluid (arrows in figure 1a) and/or the discharge heat transfer fluid (arrows in figure 1b) through the regenerator.

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.

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

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

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 that is aqueous. The invention is in fact particularly advantageous under these conditions.

However, the invention is not limited to particular heat transfer fluids.
Preferably, in particular when the charge and discharge heat transfer fluids are of the same type and when the charge heat transfer fluid has undergone 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 m³, or even higher than 100 000 m³.

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

The regenerator 10, shown in greater detail in figure 2, comprises a bed 11 of energy storage media 12 placed in a chamber 14.

Bed of energy storage media

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.

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 "metallurgie extractive de l'aluminium", reference M2340, editions T.I., published January 10, 1992 (in particular chapter 6 starting on page M2340-13 and figure 7 on page M2340-15). 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.

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

- 25% < Fe₂O₃ < 90%, or even Fe₂O₃ < 85%, or even Fe₂O₃ < 80%, or even Fe₂O₃ < 75%, or even Fe₂O₃ < 70%, or even Fe₂O₃ < 65%, or even Fe₂O₃ < 60% and/or preferably Fe₂O₃ > 30%, preferably Fe₂O₃ > 35%, preferably Fe₂O₃ > 40%, or even Fe₂O₃ > 45%, or even Fe₂O₃ > 50%, and
- 5% < Al₂O₃ < 30%, preferably Al₂O₃ < 20%, and
- CaO < 20%, and
- TiO₂ < 25%, preferably TiO₂ < 20%, preferably TiO₂ < 15%, and
- 3% < SiO₂ < 50%, or even SiO₂ < 40%, or even SiO₂ < 30%, or even SiO₂ < 20%, or even SiO₂ < 15%, and
- Na₂O + K₂O < 10%, or even Na₂O + K₂O < 5%, and
- Fe₂O₃ + Al₂O₃ + CaO + TiO₂ + SiO₂ + Na₂O + K₂O > 80%, preferably Fe₂O₃ + Al₂O₃ + CaO + TiO₂ + SiO₂ + Na₂O + K₂O > 85%, or even Fe₂O₃ + Al₂O₃ + CaO + TiO₂ + SiO₂ + Na₂O + K₂O > 90%, or even Fe₂O₃ + Al₂O₃ + CaO + TiO₂ + SiO₂ + Na₂O + K₂O > 95% and
- other oxides: complement to 100%.

Preferably, the energy storage media consist of over 90%, preferably over 95%, preferably over 99% oxides.

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.

The shapes and dimensions of the energy storage media 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.

The energy storage media 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 US 6,889,963 and/or described in US 6,699,562.

The energy storage media are assembled in the chamber in order to constitute the bed.

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).

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.

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, and preferably higher than 7000 T.
**Chamber**

The chamber 14 is provided with a top opening 16 and a bottom opening 18.

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

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.

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.

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.

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.

The shell 20 is insulated internally by an insulating layer 24 according to the invention, in contact with the energy storage media.

The wall of the shell consists of an upper wall 30, a lower wall 32 and a side wall 34.

Preferably, the insulating layer extends over more than 70%, preferably more than 80%, preferably more than 90%, preferably more than 95%, preferably over substantially 100%, of the area of the side wall of the shell, or even the total area of the shell.

The minimum thickness, or even the average thickness, of the insulating layer (measured from the interior of the regenerator to the exterior of the regenerator) is preferably higher than 100 mm, preferably higher than 150 mm, preferably higher than 200 mm, preferably higher than 300 mm, preferably higher than 400 mm, and/or lower than 700 mm, preferably lower than 600 mm.

Preferably, the insulating layer is 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 5%, that is to say that the energy restored at the end of the discharge phase is higher than 95% of the total energy injected into the regenerator at the end of the charge phase. Preferably, these
losses are lower than 3%, preferably lower than 1%, preferably, the time between the end of a charge phase and the beginning of the discharge phase being shorter than 48 hours, preferably shorter than 24 hours.

The thermal resistance of the insulating layer is preferably higher than 1 m².K/W, preferably higher than 1.2 m².K/W, or even higher than 1.3 m².K/W.

The insulating layer comprises a structure, made of a "structural material", defining a plurality of cavities which are at least partly filled with an insulating material.

During the operation of the regenerator, and in particular when a heat transfer fluid is humid air, the condensates of the moisture in the air corrode the materials of the regenerator. Even more, at high pressures, the water present in the air can condense and mix with the other condensates or pollutants present. The latter may thus make the water acidic and hence corrosive.

Besides the stresses imposed by the heat transfer fluids, and particularly the potentially corrosive environment, the energy storage media impose physical stresses on the chamber wall with which they are in contact, and in particular stresses resulting from their thermal expansion and the penetration force which they generate when placed in bulk in the regenerator.

The structure advantageously forms a protective barrier for the insulating material. Advantageously, the choice of the insulating material is therefore no longer imposed by the environment prevailing in the regenerator.

The configuration of the structure, the type of structural material, the number of cavities, the volume of the cavities, the bulk density of the cavities (number of cavities per m³), the orientation of the cavities, the chemical composition of the insulating material, the physical structure of the insulating material, the density of the insulating material and the filling ratio are preferably adapted to the local insulation stresses in the regenerator. A regenerator according to the invention can thus advantageously comprise an insulating layer that has a perfectly adapted thermal profile, which therefore serves to optimize the cost of the regenerator.

Structure

Structural material

The structural material is preferably a ceramic material.

The structural material preferably consists of oxides for more than 90%, preferably more than 95%, preferably more than 99%, preferably substantially 100% of its mass.

Preferably, the oxides of the structural material are polycrystalline.
In an embodiment, the structural material has the following chemical analysis, in weight percent based on the oxides and for a total of 100%:

- \( \text{Fe}_2\text{O}_3 > 25\% \), preferably \( \text{Fe}_2\text{O}_3 > 30\% \), preferably \( \text{Fe}_2\text{O}_3 > 35\% \), preferably \( \text{Fe}_2\text{O}_3 > 40\% \), or even \( \text{Fe}_2\text{O}_3 > 45\% \), or even higher than 50\%, and/or lower than 85\%, or even lower than 80\%, or even lower than 75\%, or even lower than 70\%, or even \( \text{Fe}_2\text{O}_3 < 65\% \), or even \( \text{Fe}_2\text{O}_3 < 60\% \), and
- \( 5\% < \text{Al}_2\text{O}_3 < 30\% \), preferably \( \text{Al}_2\text{O}_3 < 25\% \), preferably \( \text{Al}_2\text{O}_3 < 20\% \), and
- \( \text{CaO} < 20\% \), and, in particular when said material is fabricated from an initial batch comprising a red mud, \( \text{CaO} > 3\% \), or even \( \text{CaO} > 5\% \), or even \( \text{CaO} > 10\% \), and
- \( \text{TiO}_2 < 25\% \), preferably \( \text{TiO}_2 < 20\% \), preferably \( \text{TiO}_2 < 15\% \), and, in particular when said material is fabricated from an initial batch comprising a red mud, \( \text{TiO}_2 > 5\% \), or even \( \text{TiO}_2 > 10\% \), and
- \( \text{SiO}_2 > 3\% \), preferably \( \text{SiO}_2 > 5\% \), or even \( \text{SiO}_2 > 8\% \), and \( \text{SiO}_2 < 50\% \), or even \( \text{SiO}_2 < 40\% \), or even \( \text{SiO}_2 < 30\% \), or even \( \text{SiO}_2 < 20\% \), or even \( \text{SiO}_2 < 15\% \), and
- \( \text{Na}_2\text{O} + \text{K}_2\text{O} < 10\% \), preferably \( \text{Na}_2\text{O} + \text{K}_2\text{O} < 5\% \), and
- other oxides < 20\%, preferably other oxides < 10\%, preferably other oxides < 5\%, preferably other oxides < 3\%.

In an embodiment, said structural material has a \( \text{CaO} \) content preferably lower than 5\%, or even lower than 3\%, or even lower than 1\%.

In an embodiment, said structural material has a \( \text{TiO}_2 \) content preferably lower than 5\%, or even lower than 3\%, or even lower than 1\%.

Preferably, \( \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{CaO} + \text{TiO}_2 + \text{SiO}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O} > 40\% \), \( \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{CaO} + \text{TiO}_2 + \text{SiO}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O} > 50\% \), \( \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{CaO} + \text{TiO}_2 + \text{SiO}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O} > 60\% \), \( \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{CaO} + \text{TiO}_2 + \text{SiO}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O} > 70\% \), \( \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{CaO} + \text{TiO}_2 + \text{SiO}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O} > 85\% \), or even \( \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{CaO} + \text{TiO}_2 + \text{SiO}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O} > 90\% \).

Preferably, the other oxides comprise for over 90% of their mass, or even consist of, an oxide selected from boron oxide, copper oxides, iron oxides other than \( \text{Fe}_2\text{O}_3 \), and mixtures thereof.

The structural material may for example be ilmenite, a clay, or a bauxite.

In an embodiment, the structural material contains more than 50\%, preferably more than 60\%, preferably more than 70\%, or even more than 75\%, or even more than 80\%, or even more than 90\% by weight of aluminum-magnesium spinel, for example \( \text{Mg}_2\text{Al}_2\text{O}_4 \), and/or steatite, and/or forsterite \( \text{Mg}_2\text{SiO}_4 \), and/or ilmenite \( \text{FeTiO}_2 \), and/or iron oxides. Preferably, the mass complement to 100% comprises, for over 90% of its mass, or even consists of, an oxide selected from boron oxide, sodium oxide, copper oxides, iron oxides, silica, alumina, and mixtures thereof, and/or
a compound of these oxides. Preferably, the mass complement to 100% comprises for over 90% of its mass, or even consists of, silica, iron oxides or mixtures thereof, and/or a compound of these oxides.

In an embodiment, the structural material is chemically substantially identical to the material constituting the energy storage media. Advantageously, the thermomechanical stresses during the thermal cycling are decreased.

The minimum thickness of structural material separating the cavities and the internal volume of the chamber wherein the energy storage media are placed is preferably higher than 2 mm, preferably higher than 5 mm. The maximum thickness of structural material separating the cavities and the internal volume of the chamber wherein the energy storage media are placed is preferably lower than 20 mm, preferably lower than 15 mm, or even lower than 12 mm.

The open porosity of the structural material is preferably lower than 20%, preferably lower than 18%, or even lower than 15%, or even lower than 10%, or even lower than 6% and/or higher than 0.5%, or even higher than 1%, or even higher than 5%.

The compressive strength of the structural material is preferably higher than 10 MPa, preferably higher than 20 MPa, preferably higher than 50 MPa.

The pyroscopic resistance of the structural material is preferably higher than 700°C, or even higher than 800°C, or even higher than 900°C, or even higher than 1000°C.

20 **Cavities**

The cavities serve to increase the number of possible forms of the insulating material. For example, the insulating material may be in the form of a powder or a fibrous mat.

The shape and number of cavities are nonlimiting.

The cavities may in particular be tubular, for example polyhedral. The axis of a tubular cavity, which defines its length, may be straight or curved.

The cross-section of a cavity (that is to say perpendicular to its axis) may be circular or not. It may, for example, be parallelepiped-shaped, in particular rectangular parallelepiped-shaped, as shown.

The cross-section of a tubular cavity may be constant along its length, particularly when it has been formed by extrusion, or not.

The cavities may be closed, blind or through cavities, preferably through cavities. "Blind" means that a cavity comprises a bottom and a side wall extending from the bottom so as to form a receptacle. Advantageously, the through cavities avoid thermal bridges and improve the thermal performance of the regenerator.
Preferably, more than 50%, more than 70%, more than 80%, more than 90%, or even 100% by number of the cavities containing insulating material are through cavities.

The cavities may also have a complex shape. For example, their surface may have bulges or roughness, in particular to limit the collapse of the insulating material.

The largest dimension of any cavity is preferably lower than 50 cm, preferably lower than 40 cm, preferably lower than 30 cm, or even lower than 20 cm and preferably higher than 2 cm, or even 4 cm.

The smallest dimension of any cavity is preferably higher than 1 cm, preferably higher than 2 cm and preferably lower than 50 cm, preferably lower than 40 cm, preferably lower than 30 cm, or even lower than 20 cm.

The cavities may or may not all have the same volume. The volume of a cavity may in particular be adapted to the insulating material, but also to its location in the regenerator.

The volume of any cavity is preferably higher than 10 cm³, preferably higher than 25 cm³, preferably higher than 50 cm³ and/or lower than 125 000 cm³, preferably lower than 100 000 cm³, preferably lower than 75 000 cm³, preferably lower than 50 000 cm³, or even lower than 25 000 cm³, or even lower than 15 000 cm³, or even lower than 10 000 cm³, or even lower than 5000 cm³, or even lower than 2000 cm³. A small cavity volume limits the maximum quantity of insulating material that the cavity can contain, and hence the risk of collapse of this insulating material.

It may be preferable to create cavities with small volumes, but completely filled, rather than larger, but partially filled cavities.

Preferably, the cavities account for over 50%, over 70%, or even over 80% or over 90% of the volume defined by the structure.

The areal density of the cavities is preferably higher than 40% and/or lower than 90%, or even lower than 80%, per square meter of insulating layer.

The bulk density of the cavities is preferably higher than 40% and/or lower than 90%, or even lower than 80% per cubic meter of insulating layer.

Preferably, over 50%, over 70%, over 80%, over 90%, or even 100% by number of the cavities are filled, at least partially, preferably completely, with insulating material.

The filling ratio of a cavity containing insulating material (that is to say the volume of the insulating material divided by the volume of the cavity) may be higher than 50%, higher than 60%, higher than 70%, higher than 80%, higher than 90%, or even, preferably, substantially 100%.

Preferably, the cavities are dimensioned and/or filled with insulating material so that the largest dimension of the void volume in any cavity is lower than 50 cm, preferably lower than...
40 cm, preferably lower than 30 cm, preferably lower than 20 cm, preferably lower than 10 cm. Preferably, the cavities are dimensioned and/or filled with insulating material so that the length of the void volume in any cavity is lower than 50 cm, preferably lower than 40 cm, preferably lower than 30 cm, preferably lower than 20 cm, preferably lower than 10 cm, the length being measured along the axis of the regenerator corresponding to the general flow direction of the charge and discharge heat transfer fluids.

In a particularly advantageous manner, the circulation of gas within the insulating layer, in particular due to the high temperature gradients, in particular along the length of the regenerator, is thereby reduced.

The cavities may have any orientation. In an embodiment, all the cavities are parallel to one another, for example in the direction of the length of the regenerator.

Preferably, the cavities are arranged so that any imaginary straight line passing through the insulating layer in the direction of the thickness of said insulating layer necessarily passes through at least one cavity.

The structure may be in a single piece, in particular if the regenerator is small.

The structure preferably consists of a bonding of shaped parts, or "structural blocks", the shape of the structural blocks not being limiting. Preferably, the structural 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.

A structural block may comprise a plurality of cavities. It may comprise at least one cavity and at least one, or even a plurality of cavity fractions. A cavity fraction of a structural block participates in the definition of a cavity after the bonding of the structural blocks.

The side wall of the regenerator may also comprise expansion joints in the insulating layer.

Preferably, the $\text{Al}_2\text{O}_3$ 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.

In a preferred embodiment, the structural blocks are fabricated and filled with insulating material before being delivered and assembled to form the insulating layer. The construction of the regenerator is thereby accelerated and is achieved at lower cost.

In an embodiment, the structural blocks are fabricated, delivered and assembled to form the structure before their cavities are filled with insulating material.

**Insulating material**

The insulating material is preferably selected from the group consisting of ceramics, polymers, and mixtures thereof. Preferably, the insulating material is a ceramic material.
Preferably, the insulating material is composed of oxides for more than 90%, preferably for more than 95%, preferably for more than 99%, preferably for substantially 100% of its mass.

Preferably, the insulating material has a chemical composition such that Fe₂O₃ + Al₂O₃ + SiO₂ + ZrO₂ + B₂O₃ + Na₂O + CaO + MgO + K₂O > 60%, preferably Fe₂O₃ + Al₂O₃ + SiO₂ + ZrO₂ + B₂O₃ + Na₂O + CaO + MgO + K₂O > 70%, preferably Fe₂O₃ + Al₂O₃ + SiO₂ + ZrO₂ + B₂O₃ + Na₂O + CaO + MgO + K₂O > 80%, preferably Fe₂O₃ + Al₂O₃ + SiO₂ + ZrO₂ + B₂O₃ + Na₂O + CaO + MgO + K₂O > 90%, in weight percent based on the oxides.

Even more preferably, the insulating material has a chemical composition such that Fe₂O₃ + Al₂O₃ + SiO₂ + B₂O₃ + Na₂O + CaO + K₂O > 60%, preferably Fe₂O₃ + Al₂O₃ + SiO₂ + B₂O₃ + Na₂O + CaO + K₂O > 70%, preferably Fe₂O₃ + Al₂O₃ + SiO₂ + B₂O₃ + Na₂O + CaO + K₂O > 80%, preferably Fe₂O₃ + Al₂O₃ + SiO₂ + B₂O₃ + Na₂O + CaO + K₂O > 90%, in weight percent based on the oxides.

Preferably, the complement to 100% is composed of oxides, preferably selected from BaO, TiO₂, P₂O₅ and mixtures thereof.

The insulating material must be adapted to the maximum temperature at which it is used. Thus, glass wool fiber cannot be used if the insulating material is exposed to a temperature above 400°C, or even above 350°C.

The thermal conductivity of the insulating material, in the insulating layer, between 20°C and 800°C, is preferably more than 20%, more than 50%, more than 100%, more than 200%, more than 300%, more than 400% lower than that of the structural material. Preferably, the thermal conductivity measured at 20°C is lower than 1 W/m.K, lower than 0.5 W/m.K, preferably lower than 0.4 W/m.K, preferably lower than 0.2 W/m.K.

In a particular embodiment, the thermal conductivity of the insulating material between 20°C and 800°C is lower than 0.5 W/m.K, preferably lower than 0.2 W/m.K, and the average thickness of the insulating layer is higher than 300 mm, preferably higher than 400 mm.

The linear thermal expansion coefficient of the insulating material, measured at 500°C, is preferably lower than 15.1 × 10⁻⁶°C⁻¹, preferably lower than 10.1 × 10⁻⁶°C⁻¹, or even lower than 8.10⁻⁶°C⁻¹.

In an embodiment, the difference between the thermal expansion coefficients of the insulating and structural materials, at 500°C, is less than 10%, preferably less than 5%, of the thermal expansion coefficient of the insulating material.

In an embodiment, the thermal expansion coefficients of the insulating and structural materials at 500°C are substantially identical. The insulation and durability are thereby improved.
In an embodiment, the structural material and the insulating material are chemically substantially identical. For example, the insulating material is a foam of the same material as the structural material.

In a preferred embodiment, the structural material is chemically substantially identical to the insulating material and to the material constituting the energy storage media.

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.

The insulating material may have any physical structure, for example rigid, powdery, or fibrous.

The insulating material may, for example, be a molten, poured or sintered product. The insulating material may in particular be a mortar, a concrete, preferably self-placing, or a mud, dry or wet. In an embodiment, the insulating material is a concrete.

The shaping of the insulating material may result from a pouring, in particular a vibratory pouring, a pressing, in particular a vibratory pressing, a cold pressing, a plastic paste pressing, or an isostatic pressing, a ramming, an extrusion, in particular a co-extrusion serving to produce the structure and to place the insulating material in a single step of the process, a granulation or a combination of these well known techniques. In an embodiment, the shaping of the insulating material results from a vibratory pouring or a pressing.

In an embodiment, the insulating material is a dry mud installed by ramming or by simple pouring.

The cavities make it possible to use an insulating material with a non-rigid structure, for example having the form of a powder or of fibers. The insulating material may also, for example, be a foam. The insulating material may have an elasticity that promotes its maintenance in the cavity in which it is placed.

Preferably, the insulating material is selected from the group formed by:
- powders, for example a dry mud, preferably comprising alumina and/or silica and/or aluminosilicates and/or zirconia and/or iron oxide Fe$_2$O$_3$ and/or metal hydroxides, preferably powders comprising an alumina + silica + zirconia + iron oxide Fe$_2$O$_3$ content higher than 60%, preferably higher than 70%, preferably higher than 80%, preferably higher than 90%, in weight percent based on the oxides;
- mixtures of fibers, such as glass fibers, rock wool fibers, alumina fibers and mixtures thereof, preferably glass fibers, rock wool fibers, even more preferably rock wool fibers;
- foams, in particular:
  - foamed concretes or mortars containing hydraulic binder, said hydraulic binder being selected from cements, preferably aluminous cements and/or
Portland cements and/or alumina cements, plaster, geo-polymers and mixtures thereof. Preferably, said concretes or mortars comprise alumina and/or silica and/or aluminosilicates and/or zirconia and/or iron oxide Fe₂O₃ and/or metal hydroxides and/or CaO, preferably said concretes or mortars comprise an alumina + silica + zirconia + iron oxide Fe₂O₃ + CaO content higher than 60%, preferably higher than 70%, preferably higher than 80%, preferably higher than 90%, in weight percent based on the oxides;
- foams comprising alumina and/or silica and/or aluminosilicates and/or zirconia and/or iron oxide Fe₂O₃ and/or metal hydroxides, preferably foams comprising an alumina + silica + zirconia + iron oxide Fe₂O₃ content higher than 60%, preferably higher than 70%, preferably higher than 80%, preferably higher than 90%, in weight percent based on the oxides;
- and mixtures thereof.

Preferably, the insulating material has the physical structure of a foam or of a mixture of fibers.

In an embodiment, the insulating material is rock wool fiber.

In an embodiment, the insulating material is a ceramic foam. All methods known to a person skilled in the art to fabricate ceramic foams may be used, in particular those involving the foaming of a slurry, or the use of a pore forming agent or an element capable of forming a gas during a heat treatment or a chemical reaction, thereby generating said foam.

In an embodiment, the insulating material is glass fiber and/or rock wool fiber and the bulk density of the insulating material is between 20 and 100 kg/m³.

In an embodiment, the insulating material is a foam, in particular a foamed concrete or a foamed mortar, and the bulk density of the insulating material is higher than 100 kg/m³, preferably higher than 500 kg/m³ and preferably lower than 2000 kg/m³, preferably lower than 1500 kg/m³.

The insulating material may or may not adhere to the wall of the cavities. For example, a solid and nonadhesive mass of insulating material may be introduced into a cavity. It is then preferable for the cavity to have the shape of a receptacle.

Preferably, the cavities are filled with the insulating material by pouring a foamed slurry or a foam precursor slurry, or by stamping, the foam being previously shaped, cut to the cavity dimensions, and then inserted therein.

Preferably, the insulating material, preferably a ceramic foam, is placed in the cavities of the structure, in particular of structural blocks, before the sintering of said structure or of said structural blocks.
**Structural blocks**

The structure may comprise, or even consist of, an assembly of structural blocks defining cells, at least a portion of the cells being filled, at least partially, with insulating material.

The structural blocks may have any shape. For example, a structural block may have the shape of a polyhedron, regular or not, preferably convex. The number of sides may in particular be between 3 and 10, preferably between 4 and 8, or even lower than 6. A structural block may in particular have the shape of a brick, for example with a parallelepiped base, optionally square or rectangular. The structural blocks may in particular have the shape of hexahedra, keystones, or wedges. They may have a radius of curvature that is preferably higher than 1 m and preferably lower than 10 m.

The cells of a structural block can be filled *in situ*, during the fabrication of the insulating layer.

For example, structural blocks having open cells at the upper side, or even at the underside, may be assembled conventionally, like bricks of a wall. The cells of a row of structural blocks are then filled before their upper side is covered with a joint, followed by the next row of structural blocks. The cavities of the insulating layer are then defined by the cells of the structural blocks.

Although this embodiment is not preferred, the structural blocks may also be assembled so that cells of various structural blocks communicate. A plurality of cells of blocks thereby define a cavity of the insulating layer. This cavity may be filled after assembling the structural blocks or, preferably, as the structural blocks are assembled, thereby ensuring a uniform filling.

In the preferred embodiment, the cells are filled with insulating material prior to the fabrication of the insulating layer.

All the cells of a given structural block may have the same shape, or they may not.

In an embodiment, the partitions separating the cells of a structural block have substantially identical average thicknesses. Preferably, the thickness of the partitions separating the cells of a structural block is substantially constant.

In another embodiment, the partitions separating the cells of a structural block have different thicknesses. For example, radial partitions, that is to say extending substantially along the direction of the thickness of the insulating layer, may have a lower thickness than the thickness of the longitudinal partitions, that is to say extending substantially perpendicular to the direction of the thickness of the insulating layer. Advantageously, the thickness of insulating material along the direction of the thickness of the insulating layer may be maximal, thereby serving to maximize the radial thermal conductivity while preserving a high compressive strength.
The minimum thickness of the partitions, preferably at least the radial partitions, is preferably higher than 2 mm, or even higher than 5 mm. The maximum thickness of the partitions, preferably at least the radial partitions, is preferably lower than 20 mm, preferably lower than 15 mm, or even lower than 12 mm, or even lower than 10 mm, or even lower than 8 mm.

In an embodiment, the thickness of the insulating layer is formed of $n$ of structural blocks, where $n$ is lower than 10, or even lower than 8, or even lower than 5.

In an embodiment, the structural blocks have different shapes and/or dimensions according to their position along the thickness of the insulating layer.

A structural block comprises at least one cell, preferably a plurality of cells.

Preferably, a structural block comprises a plurality of cells along its thickness, that is to say, after assembly, from the interior of the regenerator to the exterior of the regenerator. In an embodiment, the cells have different shapes and/or dimensions and/or a different ratio of filling with the insulating material and/or contain different insulating materials according to the position of said cells along the thickness of the structural block and/or according to the position of the structural block in the regenerator.

For example, the insulating material of the cells close to the interior of the regenerator may be a ceramic foam or a foamed concrete or a foamed mortar withstanding the high temperatures that prevail inside the regenerator, while the insulating material of the cells close to the exterior of the regenerator may be a polymer foam or a mixture of glass fibers.

In an embodiment, the filling ratio of the cells is a function of the distance of the cell from the interior of the regenerator. In an embodiment, the cells located nearest to the interior of the regenerator have a higher filling ratio than that of the other cells. In an embodiment, the latter are not filled with insulating material.

Figure 3a shows a plan view of an example of a hexahedral structural block 50 bounded laterally by a wall of a structural block 51 consisting of a portion of internal wall 52, intended to be in contact with the inside volume of the chamber, a portion of external wall 54, intended to be in contact with the shell of the chamber and opposite the portion of internal wall 52, and two portions of side wall 55 and 56, connecting the portions of internal wall 52 and external wall 54, intended to be joined, by means of a joint, to adjacent blocks.

The structural block 50 also comprises a radial reinforcing partition 57, a longitudinal reinforcing partition 58, and cavity partitions 60, defining, optionally with the radial and longitudinal partitions, internal 62a and external 62b cavities. The thickness of the cavity partitions 60 is lower than that of the wall of a structural block 51 and of the radial and longitudinal reinforcing partitions.

The portion of internal wall 52, portion of external wall 54, portions of side wall 55 and 56, radial reinforcing partition 57, longitudinal reinforcing partition 58, and cavity partitions 60 all
extend parallel to the axis \( Y \) of the structural block 50, perpendicular to the plane of the sheet. The radial reinforcing partition 57 perpendicularly intersects the longitudinal reinforcing partition 58, along the \( Y \) axis.

The internal cavities 62a, which are tubular with a square cross-section, are arranged in four rows extending parallel to the portion of internal wall 52, between the portion of internal wall 52 and the longitudinal reinforcing partition 58. All the internal cavities 62a or only a portion of the internal cavities 62a, preferably all the internal cavities 62a, are partially or completely, preferably completely, filled with a first insulating material, not shown.

The external cavities 62b, which are tubular and have a rectangular cross-section, are arranged in two rows extending parallel to the portion of external wall 54, between the portion of external wall 54 and the longitudinal reinforcing partition 58. All the external cavities 62b or only a portion of the external cavities 62b, preferably all the external cavities 62b, are partially or completely, preferably completely, filled with a second insulating material, not shown, identical to or different from the first insulating material.

Preferably, the internal cavities 62a and external cavities 62b are blind, one of their ends being blocked by a plug, preferably closed, each of their ends being blocked by plugs, not shown.

Figure 3b shows another example of a hexahedral structural block 50' which differs in particular from the structural block 50 by the number, shape and arrangement of the cavities 62'. The cavities 62', having a rectangular cross-section, extend parallel to the portions of internal wall 52' and external wall 54'. They are not aligned in the direction of the thickness of the insulating layer, but offset in pairs, preferably by a half-length of cavity.

In the prolongation of the cavities 62', cells 64', in the shape of a cavity fraction, for example in the shape of a half-cavity, are arranged in the portions of side wall 55' and 56'. During the assembly of the structural blocks 50', the cells 64' of two adjacent structural blocks may be arranged facing one another in order to form cavities.

This embodiment serves advantageously to limit the "thermal bridges" between two adjacent structural blocks. In fact, an imaginary line can no longer cross the insulating layer, in the direction of its thickness, without passing through a cavity.

In an embodiment, the cavities formed by placing cells 64' of two adjacent structural blocks facing each other are filled with insulating material after the assembly of these structural blocks.

In an embodiment, the cells 64' are filled with insulating material before the assembly of the structural blocks. Preferably, the insulating material then adheres to the surface of the cells 64'.
**Examples**

The following examples are provided for illustrative purposes and are nonlimiting.

The chemical analyses are carried out by X-ray fluorescence.

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

The pyroscopic resistance is determined according to standard ISO 1893 (collapse under load).

The thermal expansion coefficient is determined according to standard EN993-19.

The thermal conductivity of the structural material is determined, at ambient temperature, according to the following standard: ASTM E1461-07.

The thermal conductivity of the insulating material is determined, at ambient temperature, according to standard NF-EN-12667.

The following assumptions were used to calculate the heat losses:
- cylindrical regenerator, of constant cross-section, diameter 5 m, and in which the bed of energy storage media has a length $L$, measured along the X axis of the regenerator, equal to 20 m;
- charge and discharge heat transfer fluids: dry air;
- type and volume of energy storage media constant;
- charge temperature 527°C, or 800 K;
- total duration of charge phase: 4 hours;
- discharge temperature 50°C, or 323 K;
- total duration of discharge phase: 4 hours;
- outer wall cooling system of the water cooling type: temperature 75°C, heat exchange coefficient 500 W/m²K.

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:

$$J = \int_0^t \int_S \Phi_T dS dt$$

In this formula:
- $S$: outer surface area of the insulating layer in m²;
- $t$: duration of a complete cycle;
- $\Phi_T$: heat flux on the outer face of the regenerator, in W/m²;
- $J$: total losses in the cycle, in J.
Comparative example 1 is a regenerator comprising a shell whereof the entire side wall is insulated by an insulating layer having a constant thickness of 420 mm, consisting of RI30 insulating bricks containing 70% Al₂O₃, sold by Distisol.

Example 2, according to the invention, is a regenerator comprising a shell whereof the entire side wall is insulated by an insulating layer consisting of openwork bricks like the one shown in figure 3b, of dimensions 20 cm x 15 cm and thickness 42 cm, the structural material being a mixture comprising 40% by weight of a clay powder having an Al₂O₃ content of 27%, an SiO₂ content of 65% and 8% of other compounds, and 60% by weight of an iron oxide powder having an Fe₂O₃ content of 78.7%, an SiO₂ content of 9%, an Al₂O₃ content of 2.9%, and a MgO content of 1.1%. The openwork bricks are shaped by an extrusion technique, known to a person skilled in the art, and sintered at a temperature of 1200°C for 4 hours. The bulk density of the cavities is 73% of the volume of the openwork brick. The thickness of the structural material separating the cavities is 5 mm for the walls oriented in the heat flux direction, and 10 mm for the walls oriented perpendicular to the heat flux. All the cavities are substantially completely filled by pouring a foamed mortar having the following chemical composition: Al₂O₃: 15%, SiO₂: 35%, Fe₂O₃: 15%, CaO: 30%, other oxides: 5%, said foamed mortar being obtained by the following method: Preparation of a slurry containing 40% CEM1 white Portland cement, 30% silica sand having a median diameter of 150 µm, 30% calcium carbonate having a median diameter of 10 µm, water in a water/Portland cement ratio of 0.6 and satixane CX90T xanthan gum sold by Cargill, in a quantity of 0.02% of the mass of water. This slurry is mixed, in a beaker having an inside diameter of 130 mm and a height of 180 mm, using a deflocculating blade having a diameter of 80 mm, whereof the bottom end is positioned at 10 mm from the bottom of the beaker, for 1 minute at a speed of 500 rpm. Sodium lauryl ether sulfate in a quantity of 2% of the quantity of water is then introduced into the slurry. The volume of slurry being at most equal to one-third of the volume of the beaker, the mixture is stirred for 30 seconds at 500 rpm, and then for 1 minute at 1500 rpm. A foamed mortar is obtained and poured into the cavities of the structure. Said mortar sets at a temperature of 22°C and 40% relative humidity.

Example 3, according to the invention, is a regenerator comprising a shell whereof the entire side wall is insulated by an insulating layer consisting of openwork bricks identical to those used in the regenerator in example 2, all the cavities being substantially completely filled by pouring a ceramic foam obtained by the following method: Preparation of a slurry containing 40% by weight of a clay powder having an Al₂O₃ content of 27%, an SiO₂ content of 65% and 8% of other compounds, and 60% by weight of an iron oxide powder having an Fe₂O₃ content of 78.7%, an SiO₂ content of 9%, an Al₂O₃ content of 2.9%, and an MgO content of 1.1%, and water in a water/quantity of dry matter ratio of 0.72 and satixane CX90T xanthan gum, sold by Cargill, in a quantity equal to 0.6% of the mass of water. This slurry is mixed using a deflocculating blade having a diameter of 80 mm whereof the bottom end is
positioned at 10 mm from the bottom of the beaker, in a beaker having an inside diameter of 130 mm and a height of 180 mm, for 1 minute at a speed of 500 rpm. W53FL Schaumungsmittel, sold by Zschimmer & Schwarz GmbH, is then introduced into the slurry in a quantity of 6% of the quantity of water. The volume of the slurry being at most equal to one-third of the volume of the beaker, the mixture is then stirred for 30 seconds at 500 rpm, and then for 2 minutes at 1500 rpm. A foam is obtained and is poured into the cavities of the structure. The combination is then sintered at 1200°C for 4 hours.

Example 4, according to the invention, is a regenerator comprising a shell whereof the entire side wall is insulated by an insulating layer consisting of openwork bricks identical to those used in the regenerator in example 2, all the cavities being substantially completely filled with unpacked rock wool fibers, having a bulk density of 80 kg/m³ after the cavity is filled.

Example 5, according to the invention, is a regenerator comprising a shell whereof the entire side wall is insulated by an insulating layer consisting of openwork bricks identical to those used in the regenerator in example 2, all the cavities being substantially completely filled by pouring an alumina foam obtained by the following method: preparation of a slurry with 24.1% by weight of water and 75.9% by weight of the mixture of alumina powders having the following composition, in weight percent based on said mixture: 39.5% T60/64 -65 Mesh tabular alumina, 7% T60/64 -325 Mesh tabular alumina, 35% CT3000 SG alumina and 18.5% A10 alumina, sold by Almatis, and sataxane CX90T xanthan gum, sold by Cargill, in a quantity equal to 0.5% of the mass of water and glycerin in a quantity equal to 5.5% of the mass of water. This slurry is mixed using a deflocculating blade having a diameter of 80 mm whereof the bottom end is positioned at 10 mm from the bottom of the beaker, in a beaker having an inside diameter of 130 mm and a height of 180 mm, for 60 minutes at a speed of 500 rpm. W53FL Schaumungsmittel, sold by Zschimmer & Schwarz GmbH, is then introduced into the slurry in a quantity equal to 10% by weight of the quantity of water. The volume of the slurry being at most equal to one-third of the volume of the beaker, the mixture is then stirred for 30 seconds at 500 rpm, and then for 2 minutes at 1500 rpm. A foam is obtained. After debinding and sintering at 1600°C for 4 hours, the foam blocks are cut to the dimensions of the cavities of the structural part and placed therein.

The results obtained are given in table 1 below:
<table>
<thead>
<tr>
<th>Example</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<tbody>
<tr>
<td></td>
<td>Structural material</td>
<td>Insulating material</td>
<td>Structural material</td>
<td>Insulating material</td>
</tr>
<tr>
<td><strong>Characteristics of regenerator insulation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type of material</td>
<td>RI30</td>
<td>Obtained with 40% clay powder + 60% iron oxide powder</td>
<td>Foamed mortar</td>
<td>Obtained with 40% clay powder + 60% iron oxide powder</td>
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<tr>
<td>Thickness of insulating layer (mm)</td>
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<tr>
<td>Open porosity (%)</td>
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<td>70</td>
<td>60</td>
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<tr>
<td>Compressive strength (MPa)</td>
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<td>350</td>
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<tr>
<td>Pyroscopic resistance (°C)</td>
<td>1650</td>
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<td>700</td>
<td>&gt;1000</td>
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<td>Thermal conductivity (W/m.K)</td>
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<td>2.5</td>
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<tr>
<td>Equivalent thermal conductivity (W/m.K)</td>
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<td>0.36</td>
<td>0.42</td>
<td>0.15</td>
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<tr>
<td><strong>Results</strong></td>
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<tr>
<td>Heat losses (W/m²)</td>
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<td>432</td>
<td>503</td>
<td>361</td>
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<tr>
<td>% decrease in heat losses compared to comparative example</td>
<td>-</td>
<td>19</td>
<td>6</td>
<td>33</td>
</tr>
</tbody>
</table>

*: comparative example Table 1
As it now clearly appears, the arrangement of the insulating material in cavities limits the gas flows within the insulating layer, thereby considerably limiting the heat losses. As shown by the results given in table 1, a regenerator according to the invention can be up to 33% more efficient than the regenerator in comparative example 1.

The invention further provides great flexibility in the design of the insulating layer. In particular, the choice of the insulating material is wider, in terms of its type, but also its form (powder, mixture of fibers, etc.). The quality of the insulation may also be easily adjusted, not only by the choice of the insulating material, but also by the number and shape of the cavities and their filling ratio.

Furthermore, the arrangement of the insulating material in cavities allows it to be kept in place without any additional means for this purpose. The fabrication of the insulating layer is thereby faster and cheaper.

The arrangement of the insulating material in cavities also reduces its collapse (for powders, foams or fibrous mixtures in particular). The effectiveness of the insulating layer is thereby enhanced.

Finally, the arrangement of the insulating material in the cavities allows their protection from the environment prevailing in the regenerator, thereby increasing the service life of the insulating layer.

Obviously, the present invention is 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.

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

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

1. A regenerator comprising a bed (11) of energy storage media (12) placed in a chamber (14), the chamber comprising a shell (20) and an insulating layer (24) placed between said shell and said energy storage media or outside said shell, the insulating layer comprising a structure defining a plurality of cavities (62a, 62b; 62'), each cavity having a volume greater than 5 cm³, at least a portion of said cavities being filled, at least partly, with an insulating material, the minimum thickness of the structural material separating the cavities and the internal volume of the chamber wherein the energy storage media are placed being higher than 2 mm.

2. The regenerator as claimed in the preceding claim, in which the structure is made of a structural material having the following chemical analysis, in weight percent based on the oxides and for a total of 100%:
   - 25% < Fe₂O₃ < 90%, and
   - 5% < Al₂O₃ < 30%, and
   - CaO < 20%, and
   - TiO₂ < 25%, and
   - 3% < SiO₂ < 50%, and
   - Na₂O < 10%, and
   - other oxides < 20%.

3. The regenerator as claimed in the preceding claim, in which the structure is made of a structural material having the following chemical analysis, in weight percent based on the oxides and for a total of 100%:
   - 25% < Fe₂O₃ < 70%, and
   - 5% < Al₂O₃ < 30%, and
   - CaO < 20%, and
   - TiO₂ < 25%, and
   - 3% < SiO₂ < 50%, and
   - Na₂O < 10%, and
   - other oxides < 20%.
4. The regenerator as claimed in the preceding claim, in which the structure is made of a structural material having the following chemical analysis, in weight percent based on the oxides and for a total of 100%:
   - $40\% < \text{Fe}_2\text{O}_3 < 60\%$, and/or
   - $\text{Al}_2\text{O}_3 < 20\%$, and/or
   - $3\% < \text{CaO}$, and/or
   - $5\% < \text{TiO}_2 < 15\%$, and/or
   - $5\% < \text{SiO}_2 < 20\%$, and/or
   - $\text{Na}_2\text{O} < 5\%$, and/or
   - other oxides $< 5\%$.

5. The regenerator as claimed in any one of the preceding claims, in which the structure is made of a structural material of which more than 50% of the mass consists of one or more of the following compounds: iron oxides, alumina, magnesia, zirconia, silica, titanium dioxide, and calcium oxide.

6. The regenerator as claimed in any one of the preceding claims, in which the structure is made of a structural material having
   - a chemical composition identical to that of the material constituting the energy storage media and/or identical to that of the insulating material, and/or
   - an open porosity lower than 20%, and/or
   - a compressive strength higher than 10 MPa, and/or
   - a pyroscopic resistance higher than 700°C.

7. The regenerator as claimed in any one of the preceding claims, in which the structure consists of a bonding of structural blocks.

8. The regenerator as claimed in the preceding claim, in which the thickness of the insulating layer is formed by a plurality of structural blocks.

9. The regenerator as claimed in any one of the preceding claims, in which the minimum thickness of the insulating layer is higher than 150 mm.

10. The regenerator as claimed in the preceding claim, in which the minimum thickness of the insulating layer is higher than 400 mm.

11. The regenerator as claimed in any one of the preceding claims, in which the thermal resistance of the insulating layer is higher than $1 \text{ m}^2.\text{K/W}$. 
12. The regenerator as claimed in the preceding claim, in which the thermal resistance of the insulating layer is higher than 1.2 m²K/W.

13. The regenerator as claimed in any one of the preceding claims, in which the insulating material has a chemical composition such that \( \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{ZrO}_2 + \text{B}_2\text{O}_3 + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{K}_2\text{O} > 60\% \).

14. The regenerator as claimed in the preceding claim, in which the insulating material has a chemical composition such that \( \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{ZrO}_2 + \text{B}_2\text{O}_3 + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{K}_2\text{O} > 90\% \).

15. The regenerator as claimed in any one of the preceding claims, in which the compound of the insulating material having the highest weight content is selected from the group consisting of corundum, spinel \( \text{MgAl}_2\text{O}_4 \), calcined clays, mullite, hibonite, aluminum titanate, bauxite and combinations thereof.

16. The regenerator as claimed in any one of the preceding claims, in which the insulating material has the physical structure of a foam or of a mixture of fibers.

17. The regenerator as claimed in any one of the preceding claims, in which more than 50% by number of the cavities containing insulating material are through cavities.

18. The regenerator as claimed in any one of the preceding claims, in which the cavities account for more than 50% of the volume defined by the structure.

19. The regenerator as claimed in any one of the preceding claims, in which more than 50% by number of the cavities are filled at least partially with insulating material.

20. The regenerator as claimed in the preceding claim, in which more than 50% by number of the cavities are filled completely with insulating material.

21. The regenerator as claimed in any one of the preceding claims, in which the ratio of the volume of the insulating material of a cavity to the volume of said cavity is higher than 50%.

22. The regenerator as claimed in the preceding claim, in which the ratio of the volume of the insulating material of a cavity to the volume of said cavity is substantially equal to 100%.
23. The regenerator as claimed in any one of the preceding claims, in which the structural material and the insulating material are chemically substantially identical.

24. The regenerator as claimed in the preceding claim, in which the structural material is chemically substantially identical to the material constituting the energy storage media.

25. The regenerator as claimed in any one of the preceding claims, comprising at least first and second cavities filled with first and second insulating materials, respectively,
   - the first and second cavities having different shapes and/or volumes and/or bulk densities and/or orientations and/or filling ratios with the first and second insulating materials and/or
   - the first and second insulating materials having different chemical compositions and/or physical structures and/or densities.

26. The regenerator as claimed in any one of the preceding claims, in which the cavities are arranged so that any imaginary straight line crossing the insulating layer in the direction of the thickness of said insulating layer necessarily passes through at least one cavity.

27. The regenerator as claimed in any one of the preceding claims, in which the weight of the bed (12) is higher than 700 tonnes.

28. A thermal installation comprising:
   - a unit producing heat energy (4), and
   - a regenerator (10) as claimed in any one of the preceding claims, 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.

29. The thermal installation as claimed in the preceding claim, in which heat transfer fluid from said unit producing heat energy (4) condenses in said regenerator (10) in the form of an acidic liquid.

30. The thermal installation as claimed in either of the two immediately preceding claims, 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.
31. The thermal installation as claimed in the preceding claim, in which said temperature is lower than 800°C and higher than 500°C.

32. The thermal installation as claimed in any one of claims 28 to 31, in which the unit producing heat energy comprises a compressor.

33. The thermal installation as claimed in any one of claims 28 to 32, 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.

34. The thermal installation as claimed in the preceding claim, in which the heat energy consumption unit comprises a turbine.