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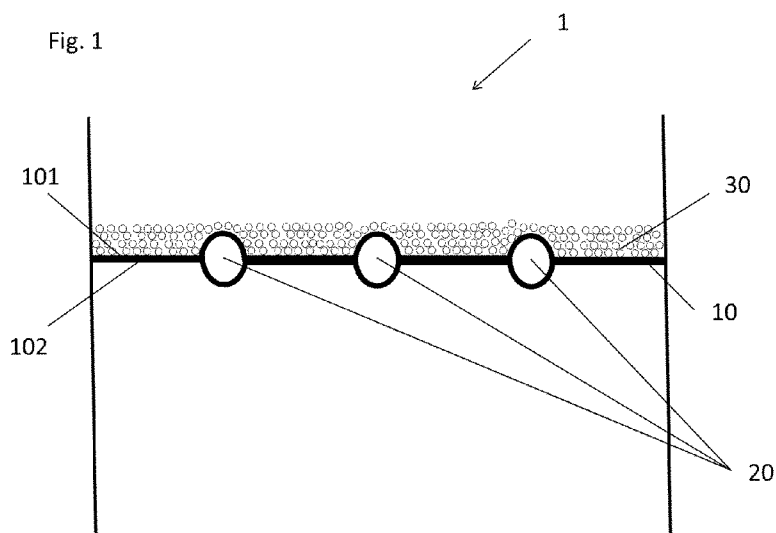
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(54) Title: HYGROSCOPIC SALT APPARATUS



(57) Abstract: A hygroscopic salt apparatus, for example a heating system, comprises a combination of: - a heat storage medium comprising a hygroscopic salt; and - a material susceptible to come into contact with the hygroscopic salt. The combination is chosen to avoid undesirable levels of corrosion and is selected from the group consisting of: - an alkaline earth chloride arranged within a porous matrix and a material selected from the group consisting of: aluminium, bronze, nickel, copper and combination thereof; - an alkaline earth bromide arranged within a porous matrix and a material selected from the group consisting of: brass, stainless steel, steel, nickel, copper, zinc, aluminium and combination thereof; - an exposed alkaline earth chloride and a material selected from the group consisting of: brass, nickel, copper and combination thereof; - an exposed alkaline earth bromide and a material selected from the group consisting of: aluminium, brass, nickel and combination thereof.



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Hygroscopic salt apparatus

[1] The present invention relates to a hygroscopic salt apparatus, for example a hygroscopic salt heating apparatus and particularly to materials for metal components, notably for a heat exchanger, for such an apparatus.

5 [2] A hygroscopic salt heating system selectively stores and releases energy by changing the atmospheric conditions to which its hygroscopic salt is subjected. Heat is released by causing hydration of a dehydrated form of the salt, for example by introducing water vapour into controlled atmospheric condition in which the salt is kept; subsequently de-hydrating a hydrated form of the salt, notably by heating, allows energy to be "stored"  
10 for release in a subsequent re-hydration. One application for such heating systems is for storage of thermal energy produced, for example by solar collectors, during the summer and subsequent controlled release of this energy to heat a building during the winter. Such a heating system should have longevity of several years, for example of at least 10, 15, 20 or 30 years; consequently the components of the system and the overall interaction  
15 between these components should be resistant to any deterioration over such durations.

[3] Unfortunately, the hygroscopic salts of interest for such systems tend to be highly corrosive with respect to metals especially when in a liquid form but also when in solid form. During a typical dehydration/hydration cycle the salt is subject to morphological changes and may undergo a partial liquefaction, particularly if atmospheric conditions are  
20 not perfectly controlled. Whilst metal parts, for example of a heat exchanger, liable to come into contact with hygroscopic salts in heating systems could be coated with, or even replaced by, a non-corrosive material such as a plastic, this would decrease their thermal conductivity and thus decrease the heat generating efficiency of the system. Increasing the thickness of such metal parts so that the amount of corrosion over the lifetime of the  
25 heating system can be tolerated brings similar disadvantages. Similarly, other metal parts cannot be simply replaced or coated without detriment.

[4] Consequently, one of the aims of the present invention is to provide a hygroscopic salt apparatus in which metal parts will withstand corrosion over the lifetime of use.

30 [5] According to one of its aspect, the present invention provides a hygroscopic salt apparatus as defined in claim 1. Additional aspects are defined in other independent claims. The dependent claims define preferred and/or alternative embodiments.

[6] According to the invention, it has surprisingly been found that particular combinations of heat medium storage hygroscopic salts, notably in specific forms, with particular materials provide a corrosion rate which renders the combination suitable for  
35 lifetime use in an apparatus, for example in a heating system. It has also surprisingly been found that the form of the hygroscopic salt is important in the selection of the heat medium storage/materials combination.

[7] The hygroscopic salt may comprise an alkaline earth bromide and/or an alkaline earth chloride; preferably the hygroscopic salt comprises strontium bromide and/or  
40 calcium chloride.

[8] The hygroscopic salt may be arranged within the pores of a porous matrix. Alternatively, the hygroscopic salt may be in an exposed form, that is to say in a form in which it is not retained within a supporting structure, for example in the form of a crystal salt. Incorporating the salt in a porous matrix to provide a composite material facilitates  
45 contact between the salt and its surrounding atmosphere; it thus facilitates heat exchange.

The porous matrix may be silicagel or activated carbon. The hygroscopic salt may be as described in UK patent application GB1411286.6 which is herein incorporated by reference.

[9] The material susceptible to come into contact with the hygroscopic salt in the apparatus may form a heat exchanger or part of a heat exchanger notably adapted to transfer thermal energy from the hygroscopic salt to a heat transfer fluid during hydration of the hygroscopic salt. The transfer fluid, which may comprise water vapour or liquid water, may circulate within the heat exchanger; the heat exchanger may comprise a metal layer supporting a plurality of metal pipes in which a heat-transfer fluid flows or two joined metallic layers which together create hollow channels in which the heat-transfer fluid flows. The material may form part of a reaction vessel, a hygroscopic salt container, a hygroscopic salt support, a hygroscopic salt conveyor, a hygroscopic salt handling apparatus or a hygroscopic salt transportation apparatus.

[10] Circumstances in which the material is susceptible to come into contact with the hygroscopic salt include where:

- there is direct contact between the salt and the material, for example where the salt in solid form lies on or over the material;
- there is direct contact between a porous matrix comprising the salt and the material, for example where a porous matrix comprising the salt in solid form lies on or over the material;
- there is the possibility of a solution comprising the salt coming into contact with the material, for example where the salt in solid form or a porous matrix comprising the salt in solid form lies on or over the material; and
- there is the possibility of a spray or vapour carrying the salt coming into contact with the material.

[11] Where the material is stainless steel, this may comprise a combination of Fe and between 10 wt% and 25 wt% Cr; it may, in addition comprise up to 21 wt% Ni. Where the material is brass, this may comprise Cu and Zn with preferably no more than 40 wt% Zn. Where the material is bronze, this may comprise Cu and Sn with preferably no more than 16 wt% Sn.

[12] The quantity of any impurities in the selected material is less than 10% wt; it is preferably less than 5% wt, more preferably less than 3% wt or 2% wt. The selected materials may be of commercial purity.

[13] The material may have a thickness which is  $\leq 5$  mm, notably  $\leq 3$  mm or  $\leq 2$  mm.

[14] The material in the pairing of the hygroscopic salt and the material may have a corrosion rate of less than  $20\mu\text{m}/\text{year}$ , preferably less than  $15\mu\text{m}/\text{year}$ , more preferably less than  $10\mu\text{m}/\text{year}$ .

[15] The apparatus may be a hygroscopic salt heating system. It may be a domestic hygroscopic salt heating system, that is to say a heating system adapted or configured to heat and/or provide hot water for a building, for example a residential building, a house, one or more flats, one or more offices. The heating system may undergo conditions so that its hygroscopic salt when at least partially hydrated may be at least partially dehydrated by subjecting it to a temperature in the range  $30^\circ\text{C}$  to  $150^\circ\text{C}$ , preferably  $40^\circ\text{C}$  to  $120^\circ\text{C}$ , more preferably  $60^\circ\text{C}$  to  $110^\circ\text{C}$ , even more preferably  $70^\circ\text{C}$  to  $100^\circ\text{C}$  during a period of at least 5 minutes, 10 minutes, 30 minutes, 45 minutes, 60 minutes or 90 minutes. The at least partially dehydrated hygroscopic salt may be stored for a period of at least 1 hour, at least 4 hours, preferably at least 4 days, more preferably at least 4 weeks,

even more preferably at least 4 months prior to contact with water to release its hydration energy. The at least partially dehydrated hygroscopic salt may be exposed to water, in vapour form, in order to rehydrate the hygroscopic salt whilst removing the heat from the hygroscopic salt at a temperature in the range 20°C to 80°C, preferably 20°C to 60°C, more preferably 30°C to 50°C. The heating system may be used to store energy prior to its subsequent release for a period of at least 168 hours (about one week), at least 672 hours (about four weeks), at least 2016 hours (about 12 weeks) or at least 4032 hours (about 24 weeks).

[16] Preferably, the hygroscopic salt is dispersed substantially homogeneously in a porous matrix but without completely filling the porosity; this allows a large amount of salt to be supported whilst facilitating accessibility for exchange of water vapour between the salt and its surrounding atmosphere. The form of grains facilitates incorporation of the material in an energy storage system and provides a large surface area which also facilitates contact between the composite material and its surrounding atmosphere. The grains may have an average diameter of at least 50µm and/or less than 3mm. The amount of hygroscopic salt in the grains with respect to the total pore volume of the porous matrix in the grains may be no more than 95%, no more than 90%, no more than 85%, preferably no more than 80%.

[17] In a preferred embodiment, the porous matrix comprises grains having a peripheral zone and a central zone, the peripheral zone of a grain being a portion of the grain extending from a periphery of the grain towards the centre of the grain for a distance of about 1/10<sup>th</sup> of the diameter of the grain, and the central zone of a grain being a portion of the grain extending from the centre of the grain for a distance of about 1/10<sup>th</sup> of the diameter of the grain towards the periphery of the grain; the peripheral zone has a peripheral zone hygroscopic metal concentration HMC<sub>p</sub> expressed as the mass percentage of metal(s) of the hygroscopic salt(s) at the peripheral zone HMP divided by the mass percentage of i) the carbon of the activated carbon or ii) the silicon of the silica gel at the peripheral zone HPP (i.e.  $HMC_p = HMP / HPP$ ); the central zone has a central zone hygroscopic metal concentration HMC<sub>c</sub> expressed as the mass percentage of metal(s) of the hygroscopic salt(s) at the central zone HMC divided by the mass percentage of i) the carbon of the activated carbon or ii) the silicon of the silica gel at the central zone HPC (i.e.  $HMC_c = HMC / HPC$ ); and the central zone hygroscopic metal concentration is greater than or equal to 0.7 times, preferably 0.8 times, the peripheral zone hygroscopic metal concentration ( $HMC_c \geq 0.7 HMC_p$ , preferably  $HMC_c \geq 0.8 HMC_p$ ).

[18] The combination of hygroscopic salt and porous matrix may be selected from the following pairings, preferably having the properties shown below:

pairing of porous matrix and hygroscopic salt	Preferred water adsorption measured between 80°C and 30°C at 12.5mbar	More preferred water adsorption measured between 80°C and 30°C at 20mbar
activated carbon and strontium bromide	at least 0.19g/g, preferably at least 0.20g/g	at least 0.19g/g, preferably at least 0.20g/g
activated carbon and calcium chloride	at least 0.28g/g, preferably at least 0.29g/g	At least 0.44g/g, preferably at least 0.45g/g,
silicagel and calcium chloride	at least 0.35 g/g, preferably at least 0.36g/g, more preferably at least 0.38g/g	At least 0.60g/g, more preferably at least 0.62g/g, more preferably at least 0.64g/g

silicagel and strontium bromide	at least 0.18g/g, preferably at least 0.20g/g, more preferably at least 0.21g/g	at least 0.25g/g, preferably at least 0.26g/g, more preferably at least 0.28g/g
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[19] An embodiment of the invention will now be described, by way of example only, with reference to the accompanying drawings of which:

Fig 1 is a schematic cross section of part of a heating system; and

Fig 2 is a cross section through a grain of composite material.

- 5 [20] The hygroscopic salt heating system 1 of Fig 1 comprises a metal heat exchanger 10 having a top plate 101 and a bottom plate 102 which are joined together so as to define a plurality of hollow channels 20 extending along and between the two plates. A flow of water in the channels evacuates heat from a layer of hygroscopic salt 30 supported on the plates and is used to supply radiators and/or a hot water system of a building either  
10 directly or via an immersion heater.

[21] Experimental conditions for studying corrosion.

- [22] A hygroscopic salt (calcium chloride or strontium bromide) having an average grain diameter of about 500µm is prepared by manually crushing grains of hygroscopic salt with a mortar and pestle during a time of about 1 minute. A metal sample having two  
15 principal dimensions of at least 10mm (for example a 10mm x 10mm plate) is suitably prepared for corrosion testing (including polishing of its corners, etching to remove existing corrosion products if necessary, cleaning with Milli-Q water and drying) and is weighted with a precision of at least 0.1mg and then placed in a glass recipient so that it is completely surrounded by the hygroscopic salt. The recipient is then placed in a  
20 calibrated climatic chamber, Heraeus Vötsch VTRK 300.

[23] For each hygroscopic salt, four climatic conditions are tested using a series of recipients each containing an individual metal sample to be tested. For each of the four tests, the recipients containing the metal samples in the hygroscopic salt are held in the climatic condition for about 30 days before being taken out and examined for corrosion.

- 25 [24] For the strontium bromide test, the conditions are:

Test conditions	Comments
Tc = 65°C, Td = 64°C (i.e. RH = 95%);	This represents a typical operating condition in which the salt is a deliquescent liquid
Tc = 65°C, Td = 33°C (i.e. RH = 20%);	This represents a typical operating condition in which the salt is mono-hydrated
Tc = 80°C, Td = 56°C (i.e. RH = 35%);	This represents an extreme temperature for the operating conditions at which a high corrosion rate would be expected and at which the salt is hexa-hydrated
Tc = 80°C, Td = 48°C (i.e. RH = 24%).	This represents an extreme temperature for the operating conditions at which a high corrosion rate would be expected and at which the salt is mono-hydrated

where Tc is the temperature inside the chamber, Td is the dew point (which is related to the relative humidity (RH) or water pressure inside the chamber).

[25] For the calcium chloride, the test conditions are:

Test conditions	Comments
Tc = 35°C, Td = 10.1°C	This low temperature Tc corresponds to a extraction of low

(i.e. RH = 22 %)	temperature heated water from the system; the low dew point corresponds to a low operating vapour pressure at which adsorption of the salt can still occur. The salt is close to deliquescence.
T <sub>c</sub> = 80°C, T <sub>d</sub> = 10.1°C (i.e. RH = 3 %)	This corresponds to a dry salt
T <sub>c</sub> = 80°C, T <sub>d</sub> = 34°C (i.e. RH = 11 %)	This corresponds to a partially hydrated salt
T <sub>c</sub> = 80°C, T <sub>d</sub> = 47.1°C (i.e. RH = 23 %).	This corresponds to extreme conditions; pure salt becomes a deliquescent liquid

[26] The climatic conditions are periodically monitored with a hygrometric and thermal sensor Testo 650.

[27] At the end of the test period, the recipients are removed. Once removed from the recipients the samples are prepared for weighing by ultrasonically cleaning in water and/or ethanol, dried and visually inspected. In cases where a significant layer of corrosion is observed the samples are also etched using the following solvents:

Metal	Cleaning Solvent	Cleaning conditions (concentration, temperature, time)
Stainless steel	HNO <sub>3</sub>	10%, 60°C, 20min
Steel	H <sub>2</sub> SO <sub>4</sub>	10%, 25°C, 5min
Copper	H <sub>2</sub> SO <sub>4</sub>	10%, 25°C, 1-3min
Brass	H <sub>2</sub> SO <sub>4</sub>	10%, 25°C, 1-3min
Nickel	H <sub>2</sub> SO <sub>4</sub>	10%, 25°C, 1-3min
Aluminium	H <sub>3</sub> PO <sub>4</sub> + CrO <sub>3</sub>	5% (H <sub>3</sub> PO <sub>4</sub> ), 20g/L (CrO <sub>3</sub> ), 90°C, 5-10min
Zinc	NH <sub>4</sub> Cl	100g/L, 70°C, 2-5min

[28] The cleaned samples are then weighted and the corrosion rate is determined by the formula described for example in ASTM G1-03:

10  $v = \frac{\Delta m}{At\rho}$ , where A is the exposed area (m<sup>2</sup>), t the exposition time (year), ρ the density of the sample (kg/m<sup>3</sup>) and Δm the difference of mass of the sample between the start and the end of the exposition.

[29] The experiment is repeated using grains of porous silicagel having the hygroscopic salt arranged within the pores of the silicagel. The porous silicagel has a specific surface area between 300 and 350 m<sup>2</sup>/g and a porous volume between 0.8 and 1.15 cm<sup>3</sup>/g

[30] For the pairing silicagel + SrBr<sub>2</sub>, the amount of strontium bromide in the grains with respect to the total weight of grains is about 48%.

[31] For the pairing silicagel + CaCl<sub>2</sub>, the amount of calcium chloride in the grains with respect to the total weight of grains is about 43%.

[32] The following corrosion rates were obtained, for each pairing metal/hygroscopic salt (in a crystal form or enclosed within the pores of a porous matrix):

Pairing	Corrosion rate ( $\mu\text{m}/\text{year}$ )	Test conditions $T_c$ ( $^{\circ}\text{C}$ )	Test conditions $T_d$ ( $^{\circ}\text{C}$ )
Brass/ $\text{CaCl}_2$	1	80	47.1
Brass/silicagel+ $\text{CaCl}_2$	18	80	47.1
Steel/ $\text{CaCl}_2$	6	80	47.1
Steel/silicagel+ $\text{CaCl}_2$	320	80	47.1
Copper/ $\text{CaCl}_2$	2	80	47.1
Copper/silicagel+ $\text{CaCl}_2$	13	80	47.1
Nickel/ $\text{CaCl}_2$	not measurable	80	47.1
Nickel/silicagel+ $\text{CaCl}_2$	not measurable	80	47.1
Zinc/ $\text{CaCl}_2$	141	80	47.1
Zinc/silicagel+ $\text{CaCl}_2$	2	80	47.1
Aluminium/ $\text{CaCl}_2$	27	80	47.1
Aluminium/ silicagel + $\text{CaCl}_2$	not measurable	80	47.1
Stainless steel 316L/ $\text{CaCl}_2$	not measurable	80	47.1
Stainless steel 316L/ silicagel + $\text{CaCl}_2$	pitting	80	47.1
Stainless steel 304L/ $\text{CaCl}_2$	not measurable	80	47.1
Stainless steel 304L/ silicagel + $\text{CaCl}_2$	pitting	80	47.1
Bronze/ $\text{CaCl}_2$	9	80	47.1
Bronze /silicagel+ $\text{CaCl}_2$	6	80	47.1
Brass/ $\text{CaCl}_2$	1	80	34
Brass/silicagel+ $\text{CaCl}_2$	11	80	34
Steel/ $\text{CaCl}_2$	4	80	34
Steel/silicagel+ $\text{CaCl}_2$	4	80	34
Nickel/ $\text{CaCl}_2$	1	80	34
Nickel/silicagel+ $\text{CaCl}_2$	not measurable	80	34
Copper/ $\text{CaCl}_2$	8	80	34
Copper/silicagel+ $\text{CaCl}_2$	4	80	34
Zinc/ $\text{CaCl}_2$	not measurable	80	34
Zinc/silicagel+ $\text{CaCl}_2$	10	80	34
Aluminium/ $\text{CaCl}_2$	1	80	34
Aluminium/silicagel+ $\text{CaCl}_2$	not measurable	80	34
Bronze / $\text{CaCl}_2$	8	80	34
Bronze / silicagel+ $\text{CaCl}_2$	7	80	34
Bronze / $\text{SrBr}_2$	33	80	34
Bronze / silicagel+ $\text{SrBr}_2$	8	80	34
Brass/ $\text{CaCl}_2$	8	80	10.1
Brass/silicagel+ $\text{CaCl}_2$	2	80	10.1
Steel/ $\text{CaCl}_2$	not measurable	80	10.1
Steel/silicagel+ $\text{CaCl}_2$	not measurable	80	10.1
Nickel/ $\text{CaCl}_2$	<1	80	10.1
Nickel/silicagel+ $\text{CaCl}_2$	1	80	10.1
Copper/ $\text{CaCl}_2$	2	80	10.1
Copper/silicagel+ $\text{CaCl}_2$	2	80	10.1



Zinc/ CaCl <sub>2</sub>	not measurable	80	10.1
Zinc/silicagel+ CaCl <sub>2</sub>	3	80	10.1
Aluminium/ CaCl <sub>2</sub>	1	80	10.1
Aluminium/silicagel+ CaCl <sub>2</sub>	1	80	10.1
Brass/ CaCl <sub>2</sub>	1	35	10.1
Brass/silicagel+CaCl <sub>2</sub>	not measurable	80	10.1
Steel/ CaCl <sub>2</sub>	2	35	10.1
Steel/silicagel+ CaCl <sub>2</sub>	1	35	10.1
Nickel/ CaCl <sub>2</sub>	not measurable	80	10.1
Nickel/silicagel+ CaCl <sub>2</sub>	1	35	10.1
Copper/ CaCl <sub>2</sub>	4	35	10.1
Copper/silicagel+ CaCl <sub>2</sub>	1	35	10.1
Zinc/ CaCl <sub>2</sub>	4	35	10.1
Zinc/silicagel+ CaCl <sub>2</sub>	3	35	10.1
Aluminium/ CaCl <sub>2</sub>	2	35	10.1
Aluminium/silicagel+ CaCl <sub>2</sub>	2	35	10.1
Steel/SrBr <sub>2</sub>	1387	80	56.1
Brass/ SrBr <sub>2</sub>	20	80	56.1
Nickel/ SrBr <sub>2</sub>	4	80	56.1
Copper/ SrBr <sub>2</sub>	117	80	56.1
Zinc/ SrBr <sub>2</sub>	70	80	56.1
Aluminium/ SrBr <sub>2</sub>	not measurable	80	56.1
Stainless steel 304L/ SrBr <sub>2</sub>	pitting	80	56.1
Stainless steel 316L / SrBr <sub>2</sub>	pitting	80	56.1
Steel/SrBr <sub>2</sub>	300	80	48.3
Brass/ SrBr <sub>2</sub>	11	80	48.3
Nickel/ SrBr <sub>2</sub>	4	80	48.3
Copper/ SrBr <sub>2</sub>	80	80	48.3
Zinc/ SrBr <sub>2</sub>	26	80	48.3
Aluminium/ SrBr <sub>2</sub>	passivation	80	48.3
Stainless steel 304L/ SrBr <sub>2</sub>	pitting	80	48.3
Stainless steel 316L / SrBr <sub>2</sub>	pitting	80	48.3
Steel/SrBr <sub>2</sub>	52	65	64
Brass/ SrBr <sub>2</sub>	2	65	64
Nickel/ SrBr <sub>2</sub>	12	65	64
Copper/ SrBr <sub>2</sub>	26	65	64
Zinc/ SrBr <sub>2</sub>	46	65	64
Aluminium/ SrBr <sub>2</sub>	passivation	65	64
Stainless steel 304L/ SrBr <sub>2</sub>	12	65	64
Stainless steel 316L / SrBr <sub>2</sub>	pitting	65	64
Steel/SrBr <sub>2</sub>	52	65	33
Brass/ SrBr <sub>2</sub>	15	65	33
Nickel/ SrBr <sub>2</sub>	4	65	33
Copper/ SrBr <sub>2</sub>	9	65	33
Zinc/ SrBr <sub>2</sub>	18	65	33
Aluminium/ SrBr <sub>2</sub>	not measurable	65	33

Stainless steel 304L/ SrBr <sub>2</sub>	pitting	65	33
Stainless steel 316L / SrBr <sub>2</sub>	pitting	65	33
Steel/silicagel+SrBr <sub>2</sub>	12	80	56.1
Brass/ silicagel+SrBr <sub>2</sub>	2	80	56.1
Nickel/ silicagel+ SrBr <sub>2</sub>	1	80	56.1
Copper/ silicagel+SrBr <sub>2</sub>	2	80	56.1
Zinc/ silicagel+SrBr <sub>2</sub>	12	80	56.1
Aluminium/ silicagel+SrBr <sub>2</sub>	2	80	56.1
Stainless steel 304L /silicagel+SrBr <sub>2</sub>	2	80	56.1
Stainless steel 316L /silicagel+SrBr <sub>2</sub>	not measurable	80	56.1

[33] The composition and purity of the metals tested was:

- Steel: low-carbon steel St37;
- Copper: commercial purity;
- Zinc: commercial purity;
- 5 - Nickel: nickel "290", 99.9% purity.
- Aluminium: aluminium AlMgSi1;
- Brass: 31% Zn and 69% Cu;
- Bronze: 94% Cu and 6% Sn, no P
- Stainless steel 304L at least 18 wt% Cr and 8 % wt Ni;
- 10 - Stainless steel 316L at least 16 wt% Cr and 10 % wt Ni.

[34] The calcium chloride salt used during the tests is a salt manufactured by Solvay and has a purity of 94%. The strontium bromide is manufactured by Alfa Aesar or Sigma Aldrich and has a purity of 99%.

- 15 [35] Suitable combinations for a heating system are pairings having a corrosion rate less than 15µm/year, preferably less than 10µm/year. If no corrosion can be measured or no corrosion is visible on the surface of the metal, the pairing is accepted. The pairing is also accepted in the case of passivation of the surface.

[36] In case of pitting corrosion, the pairing is rejected, notably because pitting corrosion creates unsuitable mechanical stress for such a system.

- 20 [37] Where a pairing of silicagel + hygroscopic salt was used, this pairing was prepared and analysed as follows.

- 25 [38] A porous matrix comprising grains of silicagel (having a specific surface area between 300 and 350 m<sup>2</sup>/g and a porous volume between 0.8 and 1.15 cm<sup>3</sup>/g) was impregnated 3 times with intervening drying by a solution of calcium chloride having a concentration of 20%. The volume of the impregnation solution used for each impregnation was equal to the pre-established porous volume of the grains being impregnated. The final amount of calcium chloride within the grains of the silicagel with respect to the total weight of the grains was measured as 42.92%.

- 30 [39] Impregnated grains were analysed using a scanning electron microscope as shown in Fig 2. Grains were imprisoned in an inert resin or matrix. This was polished to provide a cross section through grains that could be analysed using an electron microscope. Chemical analysis was obtained using an EDX analyser provided with the scanning electron microscope. During sample preparation and analysis it was ensured:
- that the planarity of the surface was sufficient to provide a quantitative chemical analysis;

- that the preparation technique did not bring any element that would interfere with chemical analyses (i.e. in the case of EDX, peaks should not overlap). For example, a conductive carbon layer should not be deposited before imaging if the composite contains activated carbon;

- 5 - that the composite material was not contaminated by any other mean, for example, the polishing media;
- that none of the elements to be measured was removed by the preparation technique.

[40] Once the sample was imaged, it was verified that no “crust” of salt was present on the outer areas of the cross section. Such a crust would imply an interface between an imperfectly impregnated core and an outer area. A check using EDX can be done in case of doubt. On Fig. 2, no such phenomenon can be observed.

[41] An analysis zone was defined across the width of a grain as an inscribed rectangle with at least three corners in contact with the grain periphery. The length of the analysis zone should be at least 1/10 of the diameter of the grain and the ratio length/width should be equal to 10. Preferably, the analysis zone passes through the centre of the grain. The analysis zone was then divided into ten identical juxtaposed squares numbered sequentially from 1 to 10, as shown in Fig. 2.

[42] Square 1 (at the periphery of the grain) defines the peripheral zone and square 5 towards the centre of the grain defines the central zone at which the concentrations were determined. Table 2 gives the elements analysed (any other element was excluded from the analysis) and the condition used to verify a “good quality of impregnation”:

[43] Table 2

Pairing	Elements analysed	Impregnation considered of good quality if:
silicagel and calcium chloride	Si, O, Ca, Cl	$\left(\frac{[Ca]}{[Si]}\right)_5 \geq 0.7 \left(\frac{[Ca]}{[Si]}\right)_1$
silicagel and strontium bromide	Si, O, Sr, Br	$\left(\frac{[Sr]}{[Si]}\right)_5 \geq 0.7 \left(\frac{[Sr]}{[Si]}\right)_1$

[44] In Table 2, [x] denotes the mass percentage of element x and the indices “1” and “5” denote measurements performed on squares 1 and 5 respectively.

25 [45] The mass percentages of Ca, Cl, Si and O were measured. On square 1, [Ca]/[Si] = 0.3255 and on square 5, [Ca]/[Si] = 0.6307.

[46] Preferably, the measurement is repeated on a plurality of grains and the average is taken.

30 [47] Thus, in this example the central zone hygroscopic metal concentration was 1.94 times the times the peripheral zone hygroscopic metal concentration (HMCc = 1.94 HMCp); this satisfies the condition HMCc ≥ 0.7 HMCp.

## CLAIMS

1. A hygroscopic salt apparatus comprising a combination of:
  - a heat storage medium comprising a hygroscopic salt; and
  - a material of a metal part of the apparatus susceptible to come into contact with the hygroscopic salt;characterised in that the combination is selected from the group consisting of:
  - an alkaline earth chloride arranged within a porous matrix and a material selected from the group consisting of: aluminium, bronze, nickel, copper and combination thereof;
  - an alkaline earth bromide arranged within a porous matrix and a material selected from the group consisting of: brass, stainless steel, steel, nickel, copper, zinc, aluminium, bronze and combination thereof;
  - an exposed alkaline earth chloride in solid form and a material selected from the group consisting of: brass, nickel, copper and combination thereof;
  - an exposed alkaline earth bromide in solid form and a material selected from the group consisting of: aluminium, brass, nickel and combination thereof.
2. An apparatus according to claim 1 wherein the apparatus is a hygroscopic salt heating system.
3. An apparatus according to claim 1 or claim 2, wherein the hygroscopic salt is arranged within grains of a porous matrix.
4. An apparatus according to any preceding claim, wherein the porous matrix is selected from the group consisting of silicagel and activated carbon.
5. An apparatus according to claim 3 or claim 4, wherein the grains have a peripheral zone and a central zone, the peripheral zone of a grain being a portion of the grain extending from a periphery of the grain towards the centre of the grain for a distance of about 1/10th of the diameter of the grain, and the central zone of a grain being a portion of the grain extending from the centre of the grain for a distance of about 1/10th of the diameter of the grain towards the periphery of the grain; wherein the peripheral zone has a peripheral zone hygroscopic metal concentration  $HMC_p$  expressed as the mass percentage of metal(s) of the hygroscopic salt(s) at the peripheral zone  $HMP$  divided by the mass percentage of i) the carbon of the activated carbon or ii) the silicon of the silicagel at the peripheral zone  $HP_p$  (i.e.  $HMC_p = HMP / HP_p$ ) wherein the central zone has a central zone hygroscopic metal concentration  $HMC_c$  expressed as the mass percentage of metal(s) of the hygroscopic salt(s) at the central zone  $HMC$  divided by the mass percentage of i) the carbon of the activated carbon or ii) the silicon of the silicagel at the central zone  $HP_c$  (i.e.  $HMC_c = HMC / HP_c$ ) and wherein the central zone hygroscopic metal concentration is greater than or equal to 0.7 times the peripheral zone hygroscopic metal concentration ( $HMC_c \geq 0.7 HMC_p$ ).
6. An apparatus according to claims 1 to 5, wherein the hygroscopic salt comprises calcium chloride.
7. An apparatus according to claims 1 to 5, wherein the hygroscopic salt comprises strontium bromide.

8. An apparatus according to any of claims 2 to 7, wherein the apparatus is a hygroscopic salt heating system configured:
- to release thermal energy at relative humidity between 2.5 and 40 % and a temperature between 20 and 80°C; and
  - 5 - to absorb thermal energy at a temperature between 30 and 150°C; particularly at a temperature between 30 and 90°C, and a relative humidity between 2.5 and 40 %.
9. An apparatus according to any preceding claim, wherein the material forms part of a heat exchanger, a reaction vessel, a hygroscopic salt container, a hygroscopic salt support, a hygroscopic salt conveyor, a hygroscopic salt handling apparatus or a
- 10 hygroscopic salt transportation apparatus.
10. A method for assessing the corrosion effect of a heat storage medium comprising a hygroscopic salt on a material comprising:
- subjecting a sample of a material to the heat storage medium in a first controlled atmosphere for a duration of at least 24 hours, the controlled atmosphere having a
  - 15 relative humidity between 0 and 100% and a temperature between 5 and 100°C;
  - subjecting a sample of the material to the heat storage medium in a second controlled atmosphere for a duration of at least 24 hours, the controlled atmosphere having a relative humidity between 0 and 100% and a temperature between 5 and 100°C;
  - 20 wherein the difference in temperature between the first and second controlled atmospheres is at least 20°C and the difference in relative humidity between the first and second controlled atmospheres is at least 20 percentage points.
11. A method according to claim 10, wherein the material comprises a metal.
12. Use of at least one of the following combinations of a heat storage medium and a
- 25 material of a metal part of a hygroscopic salt apparatus:
- an alkaline earth chloride arranged within a porous matrix and a material selected from the group consisting of: aluminium, bronze, nickel, copper and combination thereof;
  - an alkaline earth bromide arranged within a porous matrix and a material selected
  - 30 from the group consisting of: brass, stainless steel, steel, nickel, copper, zinc, aluminium, bronze and combination thereof;
  - an exposed alkaline earth chloride in solid form and a material selected from the group consisting of: brass, nickel, copper and combination thereof;
  - an exposed alkaline earth bromide in solid form and a material selected from the
  - 35 group consisting of: aluminium, brass, nickel and combination thereof,
- in the hygroscopic salt apparatus for reducing corrosion of the metal part of the hygroscopic salt apparatus comprising the material.

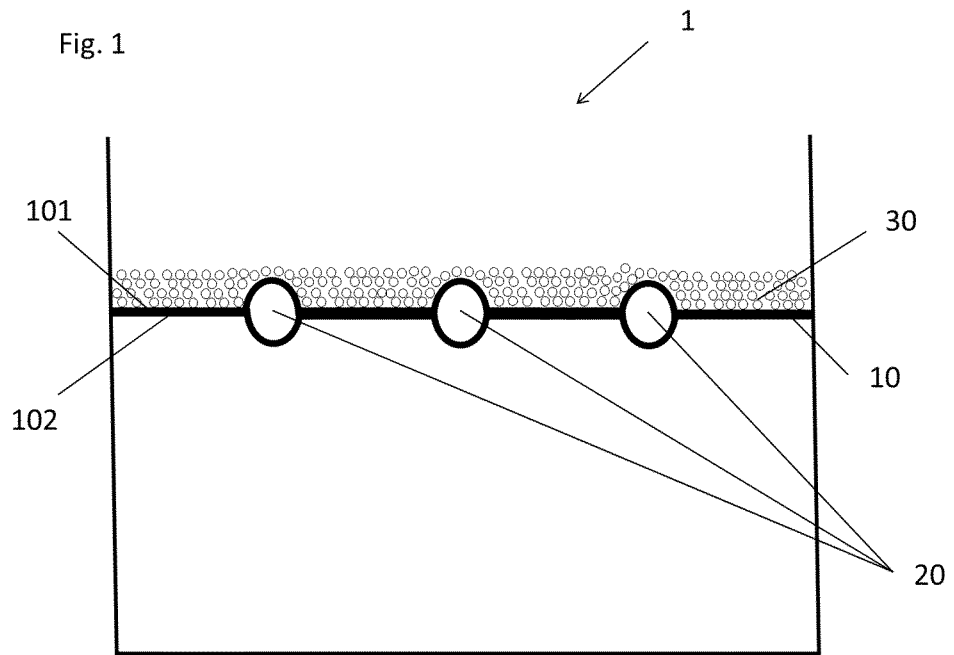
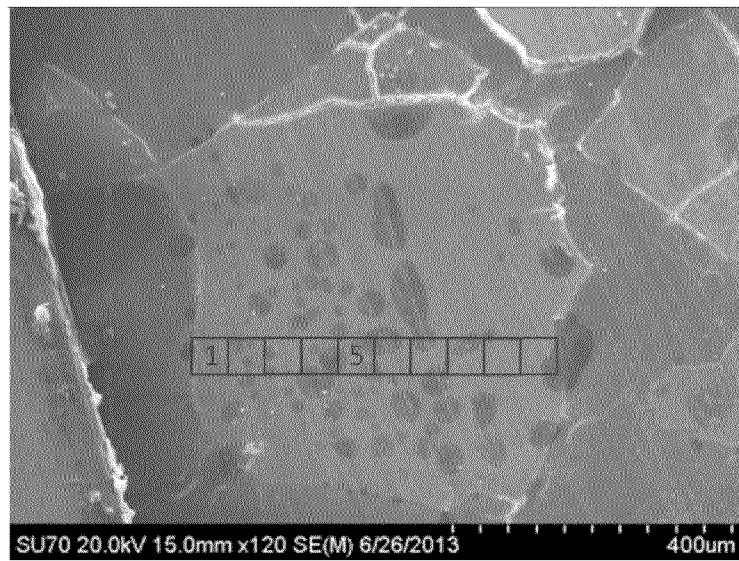


Fig 2



INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2015/072700

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C09K5/06  
ADD.  
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED  
Minimum documentation searched (classification system followed by classification symbols)  
C09K F28D

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

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

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Y	column 2, line 55 - column 3, line 19; column 3, line 60 - column 4, line 4	3-5
X	US 2013/105727 A1 (RIEGER RALPH [DE] ET AL) 2 May 2013 (2013-05-02) paragraphs [0001], [0078], [0079], [0091], [0094]	1,2,6-9, 12
X	CN 102 878 838 A (DONGGUAN HANHONG AIFA ELECTRONIC TECHNOLOGY CO LTD) 16 January 2013 (2013-01-16) embodiment 1	1,2,6,8, 9,12
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Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search  22 January 2016	Date of mailing of the international search report  05/02/2016
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Kappen, Sascha

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2015/072700

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	----- WU ET AL: "Effects of impregnating variables on dynamic sorption characteristics and storage properties of composite sorbent for solar heat storage", SOLAR ENERGY, PERGAMON PRESS. OXFORD, GB, vol. 81, no. 7, 26 June 2007 (2007-06-26), pages 864-871, XP022131859, ISSN: 0038-092X, DOI: 10.1016/J.SOLENER.2006.11.013 abstract	1-12
A	----- US 4 291 755 A (MINTO WALLACE L) 29 September 1981 (1981-09-29) column 2 line 60 - column 3, line 10; figure 2	1-12
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