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(54) **Title:**
HEAT TRANSFER INTERFACE

(57) **Abstract:**
Embodiments of the invention provide systems and methods for heat management systems at temperatures in the range of 1200 C to 1,3000 C. The systems consist of various heat transfer chambers configured such that they contain heat transfer devices that are spherical, cylindrical or have other shapes, and that absorb heat within a broad range of temperatures, and return such heat at constant temperature over long periods of time.

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(54) **Title**: HEAT TRANSFER INTERFACE

Figure 8a

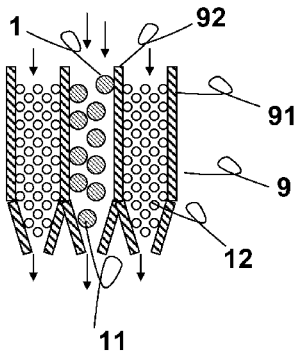
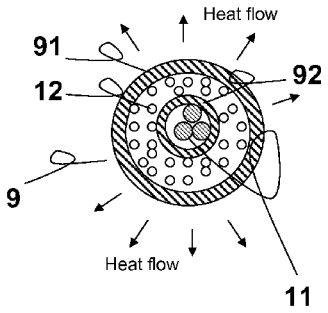


Figure 8b



(57) **Abstract**: Embodiments of the invention provide systems and methods for heat management systems at temperatures in the range of 120^0 C to 1,300^0 C. The systems consist of various heat transfer chambers configured such that they contain heat transfer devices that are spherical, cylindrical or have other shapes, and that absorb heat within a broad range of temperatures, and return such heat at constant temperature over long periods of time.

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HEAT TRANSFER INTERFACE

[0001] This invention relates to the field of heat management. In particular, embodiments of the invention relate to systems and methods of storing heat from industrial operations, and recovering such heat at constant temperature over long periods of time.

BACKGROUND

[0002] Many industrial operations today generate large amounts of waste heat, which is dissipated in evaporation towers (i.e., cooling towers), transferred to cooling water, converted into steam, or wasted to the surrounding environment. Furthermore, numerous industrial activities are intermittent in nature, so the heat generated in those operations is not continuous but only lasts for a limited time, and the temperature of those heat sources varies greatly, thus making heat recovery and heat recycling difficult and cumbersome. As a result, large amounts of energy are routinely wasted into cooling water streams, low-grade steam, or simply dissipated, thus making such industrial operations more energy-intensive than necessary.

[0003] Furthermore, many exothermic polymeric reactions in the petrochemical industry require precise temperature control, which is commonly achieved using double-walled reactors with cooling water. However, even though such reactors utilize large volumes of cooling water in the outer shell and turbulence, temperature control is difficult because heat is generated throughout the inner reactor volume and away from the cooling wall. Moreover, those cooling systems generate large volumes of cooling water at temperatures that are too small for effective heat recovery. As a result, those petrochemical operations waste significant amounts of heat and water, and they incur substantial costs in water treatment facilities before discharging such waste.

[0004] Molten salt systems have been developed to store heat at high temperatures, and are used primarily with solar concentrators. Such systems rely on the heat of melting which is typically much larger than the specific heat per unit of mass, and are able to release that heat continuously upon solidification or freezing. Sodium metal is also used for heat storage at higher temperatures, although in the case of sodium heat storage occurs mainly by heating the liquid sodium to higher temperature. Conventional molten salt systems and molten sodium systems

suffer from two major problems: what to do when there is a system failure and the salt or sodium freezes, and the need for pumping a semi-viscous media at high temperatures.

[0005] Accordingly, there is a need for an inexpensive heat-transfer media that can absorb heat at high temperature, can deliver such heat at constant temperature over a long period of time, that requires little or no maintenance and is reliable, and that can be easily manipulated even though the heat transfer media is frozen.

[0006] There are numerous technologies related to the management or storage of energy or heat using molten salts. However, the vast majority of these technologies offer little relevance to the present invention because they involve different functionalities. Thus, many relate to ion exchange resins, some to polymer systems, and some to thermoplastics, all of which involve organic polymers which are notorious for their susceptibility to thermal degradation at relatively moderate temperatures; others relate to underground heat treatment of hydrocarbon deposits and materials that are seldom encapsulated, or refer to phase change inks, toner compositions, and imaging systems. Some technologies relate to pharmaceuticals or biological systems, while others relate to flame or fire retardants, all of which bear little relevance to heat management or storage systems using phase change salts.

[0007] Many technologies employ phase change materials that are primarily salts, and many employ eutectic compositions of various salts, but they are seldom encapsulated, and thus they share the problem of freezing upon solidification.

[0008] Some technologies relate to energy storage systems based on phase change materials, and employ heat pipes in connection with such heat storage systems that include heat exchangers. Others employ phase change materials that are compacted in powder form and encapsulated by a rolling process. However, the normal problems encountered with the use of heat exchangers using molten salts are exacerbated, and the encapsulation methods employed involve expensive manufacturing and are restricted to simple shapes.

[0009] Other technologies employ hydrated metal nitrates that minimize density changes between the solid and liquid phases. However, hydrated salts lose the water of hydration readily upon heating, and such chemical changes typically occur at or before reaching the melting point of those substances. As a result, any free water is likely to evaporate, leading to pressure build up within any enclosure. Accordingly, key features of these technologies make them inappropriate for use in the applications described above.

[0010] Some technologies involve the use of crystallization inhibitors, so as to depress the temperature of solidification of phase change materials, while others employ similar systems that use a separate crystal nucleator.

[0011] Other technologies relate to methods of storing heat within a broad range of temperatures by using various phase change salt materials and a porous support structure. However, a common difficulty in all such phase change systems is the lack of flowability, that is, the fact that as the phase change material freezes, it stops flowing.

[0012] Still other technologies employ describe anhydrous sodium sulfate and similar phase change salts in connection with a heat exchanger configured to provide uniform heat distribution throughout the phase change materials. However, the common deficiency of such systems is the same described earlier, namely the fact that upon freezing such materials completely lose flowability.

[0013] Other methods employ heat pipes and mechanisms for scraping an eutectic of salt from the pipes, while molten salt provides the heat for boiling water. However, eutectic compositions present the problem that such salt mixtures tend to exhibit greater solubilities for materials that enclose the phase change salt.

SUMMARY

[0014] Embodiments of the present invention provide an improved method for heat management, one that allows for the rapid capture of heat at temperatures in the range of 120° C to 1,300° C from a variety of heat sources, and the subsequent release of such heat at constant temperature for a long period of time. The system can include an inner heat transfer medium encapsulated in an outer container that can cylindrical, spherical, or other shape, and that is inert with respect to the heat source. The heat transfer medium can include salts, metals, or ceramic compositions and is capable of removing heat by absorbing the heat of fusion from a heat source. The encapsulating container can include a metal, plastic, or ceramic composition that is non-reactive with respect to the heat source and non-reactive with respect to the heat transfer medium. In embodiments of the system, the size and shape of the encapsulating container is determined by the nature and chemical characteristics of the heat source, and by the heat transfer requirements in terms of heat removal or release per unit volume and per unit of time.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIGS. 1a and 1b are elevation views of two embodiments of encapsulated heat transfer devices.

[0016] FIGS. 2a and 2b are embodiments of heat transfer devices with inner coatings.

[0017] FIGS. 3a and 3B are elevation views of heat transfer devices with inner and outer coatings.

[0018] FIGS. 4a and 4b show two possible embodiments of heat transfer devices inside different heat transfer reactor configurations.

[0019] FIG. 5a is a schematic diagram of a double-walled petrochemical reactor chamber.

[0020] FIG. 5b is a simplified petrochemical reactor with randomly dispersed heat transfer devices.

[0021] FIG. 6 is a schematic diagram of a steel basic oxygen converter with a heat recovery chamber.

[0022] FIG. 7 is a schematic diagram of a two-pass boiler system with a heat recovery chamber.

[0023] FIGS. 8a and 8b are elevation and plant views of a coaxial heat recovery double chamber with heat transfer devices.

DETAILED DESCRIPTION

[0024] Embodiments of the invention are disclosed herein, in some cases in exemplary form or by reference to one or more Figures. However, any such disclosure of a particular embodiment is exemplary only, and is not indicative of the full scope of the invention.

[0025] Embodiments of the invention include systems, methods, and apparatus for heat management, recovery and recycling from a variety of industrial operations. Preferred embodiments provide a broad spectrum of heat absorption chambers that operate within the temperature range of 120° C and 1,300° C, and that provide for fully automated heat recovery at temperatures similar to that range over several hours, days or months without user intervention. For example, systems disclosed herein can run without user control or intervention for 2, 4, 6, 8, months, or longer. In preferred embodiments, the systems can run automatically for 1, 2, 3, 4, 5, 6, 7, 8 years, or more.

[0026] Embodiments of the invention provide for encapsulated heat transfer devices of various shapes and sizes to enter and exit heat transfer chambers at a rate commensurate with the amount of waste heat available and its temperature. Thus, the encapsulation of heat transfer devices into rigid, impervious enclosures allows such devices to flow either propelled by gravity of mechanical systems regardless of the state of the enclosed material, which typically is a salt or mixture of salts, thus providing for flowability. When heat is available, it is readily absorbed by the phase change material being encapsulated, which first heats until reaching it melting point, and then continues to absorb the heat of fusion until all of the encapsulated material becomes molten. When heat is required, the encapsulated material is transferred to another heat transfer chamber where the molten phase change material begins to solidify, thus releasing the same heat of fusion that was previously absorbed.

[0027] Heat transfer chambers can be of any shape and size that is compatible with the amount of heat available, the length of time such heat is available, and its temperature. Those three variables determine the size and shape of the heat transfer devices being used, so that they will have a residence time in the transfer chamber equal to that of heat being available, and their mass of phase change material will be adequate to the amount of heat and temperature available.

[0028] Important characteristics of the heat transfer chambers is that they allow the movement of heat transfer devices in and out of such chamber, such as by gravity flow, although other forms of mechanical transport may be employed.

[0029] Important characteristics of the heat transfer devices are that they be durable, inexpensive to fabricate, and thermally effective. Durability requires lack of chemical interaction between the enclosure material of the device and the inner phase change material. Inexpensive manufacture requires that the enclosed phase change material be encapsulated in impervious containers that are easy to fabricate, such as crimped metal cylinders, metallic or ceramic spheres, and the like. Thermal effectiveness requires that the thickness of the enclosing material be small and thermally conductive, and that it will not react chemically to either the external environment providing the heat, or the internal environment of the phase change material.

[0030] In preferred embodiments, such as those shown in Figures 1A and 1B, the heat transfer device (**1**) consists of a cylinder or sphere comprising enclosing material (**2**) or similar shape that is filled with phase change material (**3**) that may be an inorganic salt or a mixture of salts. The cylinder or sphere is made of a metal, such as copper or aluminum, or

similar inexpensive metal. In other embodiments, the enclosing material (**2**) may be a thin ceramic or polymer material that is made thermally conducting by incorporating metallic powders or shavings. In preferred embodiments, the enclosing material (**2**) consists of a crimped aluminum, copper or similar metal tube, a welded tube, or a tube or similar shape fitted with a screw cap.

[0031] Figures 2a and 2b illustrate an alternative embodiment of a heat transfer device (**1**) in which the inner surface of the enclosing material is coated with an inert substance (**21**) that is chemically non-reactive with the enclosing materials (**2**) or with the phase change material (**3**). As used in this application, "non-reactive" encompasses both completely non-reactive materials and materials that do react chemically, but in which the reaction is so slow or slight that it has no appreciable affect on the chemical properties of the materials or the structure of the heat transfer device. Suitable coatings include electrodeposited metals and alloys, paints, ceramic compositions, or polymers. Examples of inexpensive coatings on copper, aluminum and similar materials include carbides, nitrides, oxides. Examples of coating methods include chemical vapor deposition, electrostatic deposition, anodizing, electrolysis, and painting. Useful information relating to corrosion and coatings is provided in *Handbook of Corrosion Engineering*, which is incorporated herein by reference in its entirety.

[0032] Figures 3a and 3b illustrate alternative embodiments of a heat transfer device (**1**) in which both the inner and outer surfaces of the enclosing material (2) are coated with inert substances (**21**) and (**31**) that are chemically non-reactive with either the enclosing material (**2**), the phase change material (**3**), or the external environment in which the heat transfer device is operating. Suitable coatings include electrodeposited metals and alloys, paints, ceramic compositions, or polymers. Examples of inexpensive coatings on copper, aluminum and similar materials include carbides, nitrides, oxides. Examples of coating methods include chemical vapor deposition, electrostatic deposition, anodizing, electrolysis, and painting.

[0033] Figures 4a illustrates one possible embodiment of a heat transfer chamber (**4**) that consists of a cylindrical configuration containing a plurality of heat transfer devices (**1**) that are arranged randomly so as to provide for sufficient porosity to the flow of a fluid media containing heat. Figure 4b illustrates another embodiment of a heat transfer chamber (**4**) that consists of a rectangular configuration containing a plurality of heat transfer devices (**1**) that are arranged randomly so as to provide for sufficient porosity to the flow of a fluid media containing heat. Other geometrical shapes used to contain the heat transfer devices are also possible. Those

skilled in the art will recognize that cylindrical or rectangular shapes are exemplary only, and that other shapes may be utilized to fit space restrictions imposed by the type of heat source in different industrial applications.

[0034] Figure 5a is a simplified diagram of a double-walled petrochemical reactor, typical of catalytic processes involving exothermic reactions. In Figure 5a, the reactor (**6**) consists of two concentric cylindrical tanks that allow cooling water to enter through ports (**62**) and exit through ports (**63**), so as to provide cooling for the exothermic heat generated in the reactor volume (**61**). Such reactors are used extensively to control reaction temperatures in the chemical industry, and are notorious for requiring large volumes of cooling water and extensive use of pumps. Figure 5b illustrates a simplified reactor configuration that consists of a reactor **(6)** comprising a single tank and a plurality of heat transfer devices (**1**) that provide for more efficient cooling of exothermic reactions.

[0035] Figure 6 illustrates heat recovery from a basic oxygen furnace (**7**) in a steel plant. Typically, those furnaces are lined with special refractories (**71**) and are initially charged with molten iron (**72**) from a blast furnace, some fluxes and some steel scrap (**73**) that serves to cool the molten iron. Once the furnace is charged, an oxygen lance (**74**) blows oxygen into the molten iron so as to oxidize the excessive amount of carbon in the molten iron, and create steel. The reaction of oxygen with the dissolved carbon in the molten iron is a highly exothermic reaction that raises the temperature of the molten charge and creates large volumes of very hot gases at temperatures that normally exceed 1,500° C. The hot gases which consist largely of CO_2 exit the furnace at the top and are collected in a hood (**75**). The hot gases carry an enormous amount of heat that is largely captured by the heat transfer devices (**1**) that are flowing inside a heat transfer chamber (**5**) such that the residence time inside the chamber precisely balances the amount of heat being produced by the hot gases.

[0036] Figure 7 illustrates heat recovery from an industrial boiler (**8**). Typically, a burner (**81**) provides the necessary heat by burning a fuel in the fire box. The hot combustion gases initially transfer heat to a plurality of high-pressure steam tubes (**82**), and subsequently to a plurality of water boiling tubes (**83**), and a pre-heater chamber (**84**), and exit through chimney (**85**). A heat transfer chamber (**5**), connected to chimney (**85**), recovers the heat contained in the hot flue gases by transferring the heat to a plurality of heat transfer devices (**1**) that move through the chamber (**5**) at a rate commensurate with the required residence time to capture the heat contained in the flue gases.

[0037] Figure 8a and 8b illustrate an elevation and a plant view of a system (9) for recovering useful heat from the heat transfer devices (**1**). In figure 8a, two concentric chambers (**91**) and (**92**) allow high temperature heat transfer devices **(11)** at very high temperature to transfer heat to lower temperature heat transfer devices (**12**), so as to prolong the period of heat recovery at lower temperatures. Thus, heat that has been captured at very high temperature but for limited amounts of time becomes available on a continuous basis at lower temperature. As will be appreciated by one of skill in the art, different configurations can be used for transferring heat from high to low temperatures, and other shapes than cylindrical or rectangular chambers may be used.

[0038] The heat transfer devices can be made of any suitable material. Exemplary materials for enclosing the phase change media include but are not limited to metal, glass, composites, ceramics, plastics, stone, cellulosic materials, fibrous materials and the like. A mixture of materials can be used if desired. One of skill in the art will be able to determine a suitable material for each specific purpose. The chosen material will preferable be capable of standing up to long term high temperature use without significant cracking, breaking, other damage, or leaching toxic materials into the environment. If desired, the differently sized devices can be made of different materials. For example, the enclosures for high-temperature heat transfer devices can be made of metals such as steel, titanium, or various alloys, and the phase change media can consist of salts that have high melting points. The chosen material can preferably be resistant to breakage, rust, or cracking due to the heating process. Table 1 lists several metals with their melting points and their heat of fusion to facilitate selection of suitable enclosure materials.

[0039] Table 1

Formula	*Melting point, C*	*Heat of fusion*	*Units*
Na	97.5	31.72	kcal/kg
S	119	9.10	kcal/kg
Sn	231.8	14.09	kcal/kg
Bi	271.3	12.22	kcal/kg
Cd	320.9	13.67	kcal/kg
Pb	327.3	5.85	kcal/kg
Zn	419.5	28.11	kcal/kg
Sb	630.5	39.42	kcal/kg
Mg	651	87.91	kcal/kg
Al	659.7	76.68	kcal/kg
Au	1063	15.05	kcal/kg
Cu	1083	32.01	kcal/kg
Mn	1220	64.02	kcal/kg
Ni	1455	70.95	kcal/kg
Co	1495	5.97	kcal/kg
Fe	1535	64.98	kcal/kg
Pd	1549.4	36.11	kcal/kg
Ti	1725	100.09	kcal/kg
Zr	1857	36.55	kcal/kg
Cr	1930	79.07	kcal/kg

[0040] Table 2 lists several salts and provides melting points arranged in ascending order, as well as the corresponding heat of fusion. The information in Table 2 serves to select suitable phase change media for different industrial applications and heat recoveries at various temperatures.

Table 2

Formula	*Melting point, C*	*Heat of fusion*	*Units*
CaCl2+6H2O	28.33333	39.55	kcal/kg
Na3PO4	36.11111	66.67	kcal/kg
BiBr3	218	11.13	kcal/kg
BiCl3	233.5	5.68	kcal/kg
SnCl2	246	16.00	kcal/kg
LiNO3	264	87.80	kcal/kg
ZnCl2	283	40.60	kcal/kg
NaNO3	310.5556	62.78	kcal/kg
KNO3	338.8889	47.22	kcal/kg
PbBr2	373	11.70	kcal/kg
CdI2	387	10.00	kcal/kg
PbI2	402	17.90	kcal/kg
LiI	450	10.60	kcal/kg
PbCl2	501	20.30	kcal/kg
Sb2S3	550	33.00	kcal/kg
Ca(NO3)2	561	31.20	kcal/kg
CdCl2	568	28.80	kcal/kg
CuCl2	620	26.40	kcal/kg
MnCl2	650	58.40	kcal/kg
NaI	651	35.10	kcal/kg
Sb2O3	656	46.30	kcal/kg
KI	686	24.70	kcal/kg
MgBr2	700	45.00	kcal/kg
Li2MoO4	705	24.10	kcal/kg
MgCl2	708	82.90	kcal/kg
BiF3	727	23.30	kcal/kg
KBr	730	42.00	kcal/kg
BaI2	740	44.22	kcal/kg
KCl	776	85.90	kcal/kg
NaCl	800	123.97	kcal/kg
LiF	842	91.10	kcal/kg
KF	846	111.90	kcal/kg
PbF2	855	7.60	kcal/kg
CdSO4	1000	22.90	kcal/kg
CdF2	1100	35.90	kcal/kg
PbS	1114	17.30	kcal/kg
PbSO4	1170	31.60	kcal/kg
Li2SiO3	1204	80.20	kcal/kg
MgF2	1266	94.70	kcal/kg
BaF2	1354.5	26.00	kcal/kg
CaF2	1360	52.50	kcal/kg
CaSiO3	1540	115.40	kcal/kg
Cr2O3	2435	27.60	kcal/kg

[0041] In addition to phase-change materials, chemical reactions involving reduction/oxidation (REDOX) can also provide heat storage and controlled heat release and, thus, can be used as media for heat transfer applications. For example, the carbonate/bicarbonate reaction typically involves a chemical change that can be reversed upon minor changes in temperature. Thus ammonium bicarbonate decomposes into ammonium carbonate when temperature changes a few degrees centigrade, and the heat of this reaction can either be absorbed or released, thereby providing a functionality similar to that of phase change materials.

[0042] As used in this application, REDOX reactions include those in which one or more electrons are exchanged, and thus encompass a broader group of chemical reactions than simply those involving oxygen as an oxidant.

[0043] Typically, the chemical reactions of interest in this application include those in which one of the reactants is an organic material. Such chemical reactions are characterized by heats of reaction that are sharply dependant on the temperature of the system

[0044] One skilled in the art will appreciate that these methods and devices are and may be adapted to carry out the objects and obtain the ends and advantages mentioned, as well as various other advantages and benefits. The methods, procedures, and devices described herein are presently representative of preferred embodiments and are exemplary and are not intended as limitations on the scope of the invention. Changes therein and other uses will occur to those skilled in the art which are encompassed within the spirit of the invention and are defined by the scope of the disclosure.

[0045] The invention illustratively described herein suitably can be practiced in the absence of any element or elements, limitation or limitations which is not specifically disclosed herein. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions indicates the exclusion of equivalents of the features shown and described or portions thereof. It is recognized that various modifications are possible within the scope of the invention disclosed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the disclosure.

WHAT IS CLAIMED IS:

1. A heat management system comprising a plurality of heat transfer particles, each consisting of an inner heat transfer medium encapsulated in an outer container that is inert with respect to the heat source, and that is capable of the rapid capture of heat at temperatures in the range of 120° C to 1,300° C from a heat source, and the subsequent release of heat at a constant temperature over a period of time.

2. The system of claim 1, wherein the heat transfer medium comprises a material selected from the group consisting of a salt, metal, and a ceramic composition and is capable of removing heat from an environment by absorbing the heat of fusion from the heat source.

3. The system of claim 1, wherein the container comprises a material selected from the group consisting of a metal, plastic, or ceramic composition that is non-reactive with respect to the heat source and non-reactive with respect to the heat transfer medium.

4. The system of claim 2, wherein the heat transfer medium has a fusion temperature within a range of 120° C - 1,300° C.

5. The system of claim 2, wherein the heat transfer medium comprises a material selected from the group consisting of a chloride, oxychloride, fluoride, sulfate, sulfite, carbonate, bicarbonate, borate, arsenate, aluminate, bromide, chromate, hydride, manganate, silicate, sulfide, titanate, telluride, selenide, oxide, hydroxide, metal, and mixtures therefrom.

6. The system of claim 2, wherein the heat transfer medium comprises a substance that has a boiling point or a decomposition temperature that is at least 100° C higher than the fusion temperature thereof.

7. The system of claim 2, wherein the heat transfer medium comprises a substance that has a very low vapor pressure at its fusion temperature.

8. The system of claim 2, wherein the heat transfer medium comprises two or more substances that chemically react at a given temperature and thereby absorb the heat of that reaction.

9. The system of claim 8, wherein the heat transfer medium decomposes at a given temperature and thereby releases the heat of reaction to the environment.

10. The system of claim 3, wherein the container comprises a material selected from the group consisting of a copper, aluminum, chromium, iron, lead, magnesium, nickel, metal alloy, high-temperature plastic such as fluorocarbon or chlorofluorocarbon, and a ceramic, such as silicate, alumina, and similar refractory composition.

11. The system of claim 3, wherein the inner surface of the container is coated with a substance that is non-reactive with the heat transfer medium.

12. The system of claim 3, wherein the outer surface of the container is coated with a substance that is non-reactive with the heat source.

13. The system of claim 9, wherein the coating of the container comprises a material selected from the group consisting of a carbide, oxide, silicate, polymer, metal, or similar non-reactive composition with respect to the heat transfer medium.

14. The system of claim 10, wherein the coating of the container comprises a material selected from the group consisting of a carbide, oxide, silicate, polymer, metal, or similar non-reactive composition with respect to the heat source.

15. The heat management system of claim 1 wherein the heat transfer particles include a plurality of phase change materials suitable for a range of temperatures, such that the system recovers heat at various constant temperatures from the particles.

16. The system of claim 13, wherein the heat source comprises waste heat from chemical reactors handling exothermic reactions.

17. The system of claim 13, wherein the heat source comprises waste heat from steel furnaces.

18. The system of claim 13, wherein the heat source comprises waste heat from industrial boilers.