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Preparation of high temperature sensible heat storage materials from reduced vanadium tailings and graphite

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Abstract

The experimental study on the preparation of high temperature (>500 °C) sensible heat storage materials (SHS) was conducted through the means of sintering method, in which vanadium tailings after carbothermic reduction used as the main matrix, graphite as the thermal conductivity modifier, and clay as the auxiliary material. The phase analysis by XRD shows that the main phases of the SHS materials without clay addition are aluminosilicate, sodium aluminosilicate, ilmenite and graphite, while additional phases of quartz and carbonate were observed if clay is added. With the graphite addition ranging from 0 to 15%, the density and hardness of the SHS materials without clay addition generally shows decreasing tendency while both properties behave increasing first and then decreasing in the SHS materials with clay addition. In addition, with increase of graphite, thermal conductivity of material without adding clay gradually increases in a range of 0.54 ∼ 1.54 W·m⁻¹·K⁻¹, while thermal conductivity of materials with adding clay remains unchanged first and then increases in the range of 0.754 ∼ 1.922 W·m⁻¹·K⁻¹. Thermal analysis shows that when the graphite content is 3 ∼ 5%, both SHS materials without or with clay have moderate specific heat capacity and high thermal capacity (>1.2 MJ m⁻³·K⁻¹) at temperate above 500 °C, and high heat storage density (>200 kJ kg⁻¹) in the temperature range of 500 °C ∼ 750 °C, indicating SHS materials prepared in this study can be considered for application in high temperature storage system.

1. Introduction

Thermal energy storage (TES) technology plays a key role to synchronize the intermittent converted solar energy by concentrated solar power (CSP) plants with the power grid demand [1–4]. Nowadays, the most mature TES technology used in current commercial CSP plants is two-tank molten salts technology up to 565 °C [5, 6]. However, this technology has many technical limitations related to the storage medium such as its high freezing temperature and its relatively high cost. In addition, it is not suitable for the future generation of CSP plants [5, 7–9], which will require high operating storage temperature (e.g. more than 650 °C according to the 2020 SunShot target [5]). Storing sensible heat in solids known as sensible heat storage (SHS) allows the highest storage temperature levels and avoids the problem of high vapour pressure of liquid media. In this scope, a single tank with low-cost solid filler materials as packed bed TES system is a promising cost-effective technology as it reduces the storage component cost by more than 35% [10, 11], and enables higher working temperature (up to 1000 °C) [8].

For the solid SHS materials suitable in high operating temperature (more than 650 °C and up to around 1000 °C [5, 8]), it should have desirable properties [2, 12]: (1) Thermophysical properties (high energy density, high conductivity, and long-term thermal stability), (2) Chemical properties (long-term chemical stability and compatibility from circumstance), (3) Mechanical properties (high compressive strength, low thermal expansion, and high mechanical
stability), (4) Economical properties (low-cost of manufacturing into suitable shapes), (5) Environmental properties: low manufacturing energy requirement and CO₂ footprint.

Previously, many researchers have been conducted to identify or develop suitable solid storage materials. The use of abundant and low cost nature rocks have been investigated because of their good thermophysical properties [13–16]. However, it has drawbacks of relatively low operating temperature, an unequal rate of contraction and expansion of the component materials [14, 15], as well as to their destructive effect (e.g. thermal ratcheting) on the storage vessel [17]. Refractories have been pay attention because of their good thermal and mechanical stability under high operating temperatures (more than 1000 °C) such as magnesia bricks and castable ceramics, but the main drawback was their high cost [18–20]. Recently, the trend of research in this topic was the valorization of industrial wastes into ceramics to be used as high-temperature (up to 1000 °C) thermal energy storage (TES) materials. Cofalit based material [21], which is the result of the vitrification process of the toxic asbestos containing wastes (ACW) inside a torch plasma, has good thermophysical properties ($\lambda = 1.4 \text{ W/(m-K)}, C_p = 1025 \text{ J/(kg-K)}, \rho = 3100 \text{ kg m}^{-3}$) for high temperature TES application. Using the same vitrification process, coal fly ashes wastes obtained from coal-fired power plant were neutralized and the obtained materials have been proved to have good thermal properties ($\lambda = 1.3–2.1 \text{ W/(m-K)}, C_p = 735–1300 \text{ J/(kg-K)}, \rho = 2600 \text{ kg m}^{-3}$) for high temperature TES up to 1000 °C [22, 23]. One drawback of these storage materials is their high cost of heat treatment at 1400 °C in the plasma torch furnace [21]. Other interesting high-temperature TES materials were obtained from the iron and steel making processes by-products known by slags such as blast furnace slags (BFS) [22], electric arc furnace slags (EAFS) [22, 24–26], ladle furnace slags (LFS) [26], and induction furnaces slag (IFS) [12]. All these slags have shown good storage properties, and their thermal stability has been demonstrated up to 1000 °C. Nevertheless, remelting of slags is mandatory when their original form is glassy, brittle, or when they should be manufactured into suitable regular shapes [25, 27].

Vanadium tailings, also known as vanadium extraction slag or vanadium leaching slag, are by-products of vanadium slag after sodium roasting and water leaching. With the demand of China’s steel industry for vanadium special steel, the usage of vanadium in steel is increasing year by year, and the production of vanadium tailings is also increasing accordingly. At present, China’s steel industry produces nearly 1 million tons of vanadium tailings every year [28]. At this stage, utilization of vanadium tailings are mainly focused on (1) recovery of valuable metals from vanadium tailings, such as recycling iron, vanadium, etc., (2) preparation of far-infrared paint, vanadium-titanium black porcelain, geopolymers and other materials [29–31]. Although recovery of elements and preparation of various functional materials have good results, the utilization rate of vanadium tailings is still low. On the contrary, a large number of vanadium tailings are discarded, which not only occupy the site, but also cause serious pollution to the surrounding soil and water environment [31]. From the chemical composition point of view, vanadium tailings contain large amount of iron (20 ∼ 30%Fe or 30% ∼ 40%Fe₂O₃) and it has high recycling value. In addition to high iron, it also contains a certain amount of fourth period elements such as titanium, manganese, vanadium, and chromium, so their oxide system has strong black coloring effect and a high solar absorption rate [32]. Besides, relatively high amount of SiO₂ (15%–20%) can guarantee good physical and chemical properties and porcelian performance [33].

According to the calculation of FactSage thermochemical software [34], the melting point of vanadium tailings is about 950 °C, which is not quite high compared to high operating temperature of TES (up to 1000 °C). The low melting point of slag is due to the high content of Fe₂O₃ in slag. If iron is selectively reduced from vanadium extraction tailings, the composition of other transition metallic oxides (mostly TiO₂, MnO, V₂O₅, and Cr₂O₃) in the slag will increase accordingly, which can not only realize the recovery of iron [35], but also form high melting point tailings with strong black coloration ability and light absorption, which may be suitable for solar energy high temperature heat storage materials. Based on the above characteristics and research ideas, the application of vanadium tailings in high temperature SHS materials can be considered. Up to now, the research on the preparation of heat storage materials by using vanadium tailings has not been reported.

Graphite itself can withstand nearly 2000 °C, and it has good thermal conductivity and good chemical stability at elevated temperatures [36], so it is very suitable to be added into heat storage materials to increase the thermal conductivity of materials. Graphite, as a good thermal conductivity modifier, has been studied in the preparation of various molten salt based phase change heat storage composite materials [37].

Based on the above background, a new process of preparing high temperature SHS materials suitable for CSP generation from vanadium tailings was proposed in the authors’ group. In the process, vanadium tailings are firstly reduced by carbothermic reduction method to obtain low Fe-bearing reduced slag system, and then the reduced slag is sintered to prepare high temperature SHS materials with auxiliary materials. By this method, not only high temperature SHS materials can be prepared, but also abundant iron can be recovered. In addition, it can solve the problem of waste resource disposal and environmental protection. In the sintering process of preparing SHS materials, vanadium tailings after iron removal by carbothermic reduction were used as the main raw material; graphite was used as thermal conductivity modifier; clay, as the main raw material of ceramics [36],
has the characteristics of easy access and low cost [38], and is used as auxiliary material. The main aim of this work is to study the feasibility of preparing SHS materials suitable for high temperature (>500 °C) CSP plant from vanadium tailings. In this paper, the phase composition, physical and thermal properties of heat storage materials with different graphite and clay content were investigated. The results revealed that material prepared from vanadium tailings as raw material is a potential sensible heat storage material.

2. Experimental

The vanadium tailings in this study were provided by an enterprise in Panzhihua, Sichuan, China and its chemical composition is shown in table 1. It can be seen from table 1 that the vanadium tailings mainly contain oxides such as Fe₂O₃, SiO₂, TiO₂ and Na₂O, accounting for about 77%; in addition, there are a small amount of MgO, CaO, V₂O₅, Cr₂O₃ and remainders such as P₂O₅, K₂O and SO₃. The main phases of vanadium tailings are typically Fe₂O₃, Fe₂TiO₅, etc [38].

2.1. Preparation of reduced slag by carbothermic reduction of vanadium tailings

The required carbon content needed in the reduction of vanadium tailings was determined theoretically based on the content of Fe₂O₃ in slag. According to the preliminary test, the molar ratio of carbon to Fe₂O₃ was determined to be 1.04. To achieve better iron recovery, Na₂CO₃ was added as a flux with mass ratio of 4% out of total mass. The vanadium tailings, reducing agent of graphite and fluxing agent of Na₂CO₃ were mixed in a total amount of 6g and spherical shape of cold isostatic pressing was carried out at 240 MPa/180 sec. Then the sample was put into a graphite crucible with a lid, which is again put into a resistance furnace and heat treated at 1200 °C for 12 h. After furnace cooling, the samples were taken out from the crucible, and surface treatment and crushing were carried out. Finally, magnetic separation was carried out by using magnetic separation tube under the condition of magnetic field intensity of 190 mT. The reduced tailings after removal of iron were dried to the following composition analysis. The chemical composition of reduced tailings is shown in table 2. As can be seen from the table, Fe₂O₃ content decreased to 4.2%, in other word, iron reduction rate reached 93%. With reduction of iron, composition of other components increases correspondingly.

2.2. Preparation of sensible heat storage material by sintering method

Two series of experiments were designed as shown in table 3. S1 series stand for the experiments for the preparation of reduced slag and graphite based heat storage materials (RSG-HSM), while S2 series stand for the experiments for the preparation of reduced slag, graphite and high SiO₂-bearing clay based heat storage materials (RSGC-HSM). The grade of graphite powder used in this study is analytically pure, and the clay is from

### Table 1. Chemical composition of vanadium tailings %.

| Na₂O | Fe₂O₃ | SiO₂ | TiO₂ | MnO | Al₂O₃ | MgO | CaO | V₂O₅ | Cr₂O₃ | others |
|------|-------|------|------|-----|-------|-----|-----|------|-------|--------|
| 9.6  | 40.1  | 17.0 | 11.0 | 6.5 | 5.4   | 3.1 | 2.4 | 1.6  | 1.1   | 2.2    |

### Table 2. Chemical composition of reduced tailings %.

| Na₂O | Fe₂O₃ | SiO₂ | TiO₂ | MnO | Al₂O₃ | MgO | CaO | V₂O₅ | Cr₂O₃ |
|------|-------|------|------|-----|-------|-----|-----|------|-------|
| 12.8 | 4.2   | 21.3 | 22.7 | 15.2| 5.3   | 4.0 | 5.4 | 7.1  | 2.0   |

### Table 3. Experimental conditions.

| Acronym                         | Series no. | Reduced slag(%) | Clay(%) | Graphite(%) |
|--------------------------------|------------|-----------------|---------|-------------|
| RSG (Reduced slag + graphite based) | S1–1       | 100             | —       | 0           |
|                                | S1–2       | 95              | —       | 5           |
|                                | S1–3       | 90              | —       | 10          |
|                                | S1–4       | 85              | —       | 15          |
| RSGC (Reduced slag + graphite + clay based) | S2–1       | 50              | 50      | 0           |
|                                | S2–2       | 48.5            | 48.5    | 3           |
|                                | S2–3       | 47.5            | 47.5    | 5           |
|                                | S2–4       | 46.5            | 46.5    | 7           |
|                                | S2–5       | 45              | 45      | 10          |
|                                | S2–6       | 42.5            | 42.5    | 15          |
Panzhihua and its composition is shown in Table 4. All ingredients were mixed in a total mass of 6 g. The proportion of graphite content was 0% – 15% and the mass ratio of tailings to clay was fixed at 1 in the case of S2 series. The mixture was put into rubber mold and pellet with diameter of 20 mm and average height of 7.5 mm.
were made at 120 MPa/6 s through cold isostatic pressing. Then the pellets were then placed in a graphite crucible with a lid and sintered at 1000 °C for 1.5 h followed by the furnace cooling.

2.3. Physical parameter measurement and performance measurement
After sintering, the sample was taken out and the surface of the sample was carefully treated, and then the sample was ground and polished. The bulk density was measured by direct reading densitometer ZMD−1, hardness was measured by digital Vickers hardness tester HVS-50, phase analysis was conducted by x-ray diffraction (XRD), thermal conductivity in the z-axis (or cylindrical axis) direction of the cylindrical sample was measured by steady-state plate method DRL-II thermal conductivity tester, and differential scanning calorimetry (DSC) analysis was performed by STA499C of comprehensive thermal analyzer.

3. Results and discussion
3.1. Phase identification
Figure 1 shows macro-morphology of the specimen. It can be seen that all samples have black color, indicating that sintered material has solar light absorption effect. In case of S2 series samples, white light-colored spot phases were observed. With increase of graphite content, the color of the matrix gradually changes from black to grey. These phenomena are due to phase evolution.

XRD patterns of heat storage materials are shown in figure 2. In S1 series materials, the main phases of S1–1 base sample without adding graphite include Na$_{6.65}$Al$_{6.24}$Si$_{9.76}$O$_{32}$, multi-element aluminum silicate, and ilmenite Fe$(\text{Mn,Mg})TiO_3$. With the addition of graphite, the corresponding peak of graphite increased significantly, while the peak of Na$_{6.65}$Al$_{6.24}$Si$_{9.76}$O$_{32}$ and Fe$(\text{Mn,Mg})TiO_3$ gradually weakened, and no new phase was observed explaining that graphite is chemically stable to the reduced vanadium tailings. For S2 series of materials, the main phases of heat storage materials without graphite include quartz SiO$_2$, NaAl$_{1.08}$Si$_{2.92}$O$_8$, and Fe$(\text{Mn,Mg})TiO_3$. When graphite is added, graphite phase and (Mg$_{0.03}$Ca$_{0.97}$)CO$_3$ were observed. Due to the overlap between the peak of SiO$_2$ and the peak of graphite phase, it could not quantitatively distinguish the evolution of the phase. However, the XRD patterns show that with the addition of graphite, the intensity of the main peak first decreases and then increases while the intensity of SiO$_2$ phase at other corresponding 2theta positions gradually decreases, indicating that the addition of graphite causes the decrease of SiO$_2$ phase.

Comparing two series of samples, the intensity of aluminosilicate and ilmenite phases in S1 series is obviously higher than that of S2 series, in which SiO$_2$ and carbonate phases are formed accordingly. It is noticed that no phase containing Cr and V elements was found from XRD analysis. Although more clear study on phase analysis is needed, Cr and V can be considered to be dissolved in the Ti or Mn containing phases due to the similarity of atomic radius between them [38].

3.2. Basic physical properties
3.2.1. Bulk density
Figure 3 shows the bulk density ($\rho$, kg m$^{-3}$) of heat storage materials with different graphite contents. With increase of graphite content, the density of S1 series samples shows decrease tendency. The density of the base
specimen (S1–1) is 2551 kg m\(^{-3}\) and the minimal value is 2270 kg m\(^{-3}\) at 10% graphite (S1–3). The decrease of density is due to the addition of low density graphite. It can be known from literature that the density of pure graphite material at room temperature is 2250 kg m\(^{-3}\) [2, 39], which is lower than that of other components in the samples, resulting in the decrease of density.

In case of S2 series materials, the density increases first and then decreases. The density is in the range of 2140 ~ 2515 kg m\(^{-3}\). When graphite content is 3%, the density of S2 series samples reached a maximum value of 2515 kg m\(^{-3}\), and then it gradually decreased. In both S1 and S2 series, the density decreases with increase of graphite content, and does not decrease when the graphite content exceeds 10%.

A comparison of densities between some typical samples prepared in present study and other high temperature storage materials is shown in Figure 4. The obtained values of RSG (S1–1&3) and RSGC (S2–1&2) bulk density fall in the range (2000 ~ 4000 kg m\(^{-3}\)) of the different reported values from literatures of TES storage materials: EAF-G (3650 kg m\(^{-3}\)) and EAF-C (4110 kg m\(^{-3}\)) [24], IFS (2583 kg m\(^{-3}\)) [12], IACW (3100 kg m\(^{-3}\)) [40], HT concrete (2250 kg m\(^{-3}\)) [26], Quartzite (2630 kg m\(^{-3}\)) [24], Basalt (3000 kg m\(^{-3}\)) [24], and CFA (1720 kg m\(^{-3}\) & CFC (2348 kg m\(^{-3}\)) [41]. Consequently, it can be concluded that the RSG&RSGC prepared in present study have a good bulk density with respect to other high temperature TES materials.

3.2.2. Hardness

The results of hardness test showed that with the increase of graphite content, the hardness of the sample showed a decreasing tendency, as shown in figure 5. The variation behavior of hardness is very similar to that of density.
The hardness of base specimen in S1 series is 350 HV, and it decreases sharply with addition of graphite content. When the graphite content is 5%, the hardness is 220 HV. At graphite content of 10%, the hardness drops to about 50 HV. The decrease of hardness may be because the addition of graphite powder hinders the adhesion of matrix components [42], thus reducing the overall hardness of heat storage materials. For the S2 series, the density is generally lower than that of S1 series. This may be due to the decrease of aluminosilicate and ilmenite phases in S2 series as discussed in 3.2.1. The maximum hardness of S2 series is 140 HV and it appears when graphite content is 3%.

Similar to the behavior of bulk density, the hardness of both RSG and RSGC materials have relatively high density at graphite content lower than 10%. In this range of graphite content (<10%), the density measured are in the range of reported values from high temperature SHS materials [2]: igneous rocks (102 ~ 310 HV) including basalt (157.6 HV), sedimentary rocks (40 ~ 158 HV), metamorphic rocks (46.5 ~ 252.7 HV) including quartzite(185.9 ~ 252.7 HV). Consequently, it can be concluded that the RSG&RSGC prepared in present study have a good hardness with respect to other high temperature TES materials.

3.3. Thermal properties

3.3.1. Thermal conductivity

The thermal conductivity of heat storage materials with different graphite content was measured at 45 °C and the results are shown in figure 6. As seen in the figure, the thermal conductivity of S1 series samples increases gradually with increase of graphite content. The conductivity of base sample (S1–1) in S1 series is 0.54 W·m⁻¹·K⁻¹, and increases to 1.54 W·m⁻¹·K⁻¹ when graphite content is 15%. In case of S2 series, thermal conductivity ranges from 0.754 W·m⁻¹·K⁻¹ to 1.922 W·m⁻¹·K⁻¹ with increase of graphite content in the range of 0 ~ 15%. For the base sample (S2–1) of S2 series, thermal conductivity is higher than that of S1–1 implying clay addition can increase thermal conductivity in a certain range. With increase of graphite content, thermal conductivity remains unchanged until graphite is 5% and then increases. This delay may be due to the evolution of internal phase of heat storage materials. As seen in figure 2, the additional phase of SiO₂ with high thermal conductivity (7.69 W·m⁻¹·K⁻¹) [39] was formed in S2–1 base sample compared with S1–1. At relatively low graphite content (less than 5%), the carbonate phase is formed in addition to SiO₂ and the formation of these phases may weaken the comprehensive thermal conductivity of the heat storage material. When the graphite content reaches a certain level, the comprehensive thermal conductivity of the material is mainly dominated by the graphite material, so it shows sharp increase tendency at graphite content is higher than 5%.

A comparison of thermal conductivity between some typical samples prepared in present study and other high temperature SHS materials is listed in table 5. Although addition of graphite can increase thermal conductivity, considering the problem that the density and hardness of the material decrease with graphite content, the graphite content should not be too much. When the content of graphite is less than 10%, the obtained thermal conductivities are 0.54 ~ 1.5 W·m⁻¹·K⁻¹. Taking average, thermal conductivity is 1.02 W·m⁻¹·K⁻¹ and it is in the range (0.7–5.7 W·m⁻¹·K⁻¹) of reported values [1, 2, 19, 21, 22, 43, 44] from high temperature SHS materials: it is higher than that of WDF (powder material produced during the steelmaking process in electric arc furnace, 0.7 W·m⁻¹·K⁻¹) and WRutF (by product of ilmenite mining, 0.7 W·m⁻¹·K⁻¹).
Table 5. Thermophysical properties of the SHS materials and SHS materials [1, 2, 19, 21, 22, 25, 45, 46].

| Designation of developed SHS material | \( \rho (\text{kg m}^{-3}) \) | \( \lambda (\text{W m}^{-1} \cdot \text{K}^{-1}) \) at room temp. | \( C_p (\text{kJ kg}^{-1} \cdot \text{K}^{-1}) \) at 500°C | \( \rho \times C_p (\text{MJ m}^{-3} \cdot \text{K}) \) at 500°C | Formulations of the used raw materials |
|--------------------------------------|-------------------------------|------------------------------------------------|---------------------------------|-----------------------------------------------|---------------------------------------------|
| Cofalit                              | 3120                          | 1.4-2.0                                        | 0.920                           | 2.870                                          | 100% cofalit                                 |
| Quartzite                           | 2630                          | 2.9-5.7                                        | 1.140                           | 2.998                                          | 100% quartzite                                |
| Basalt                              | 3000                          | 1.2-2.3                                        | 0.920                           | 2.760                                          | 100% basalt                                   |
| EAF-Slag 1                          | 3430                          | 1.3-2.1                                        | 0.930                           | 3.200                                          | 100% EAF slag                                 |
| EAF-Slag 2                          | 3770                          | 1.3-2.1                                        | 0.910                           | 3.438                                          | 100% EAF slag                                 |
| CS_P                                | 3600                          | 0.8                                            | 1.188                           | 4.277                                          | 100% copper slag P                           |
| CS_B                                | 3700                          | 1.1                                            | 0.999                           | 3.696                                          | 100% copper slag B                           |
| IB                                  | 2100                          | 3-4                                            | 0.850                           | 1.785                                          | 100% by-product of potash production         |
| WDF                                 | 3967                          | 0.7                                            | 1.200                           | 4.760                                          | 100% by-product from EAF                     |
| WRutF                               | 4154                          | 0.8                                            | 1.085                           | 4.507                                          | 100% by-product of ilmenite mining           |
| CBPC_B                              | 2828                          | 1.6                                            | 1.015                           | 2.870                                          | 80% phosphate cement + 20% CS_B              |
| CBPC_P                              | 2804                          | 1.5                                            | 1.230                           | 3.449                                          | 80% phosphate cement + 20% CS_P             |
| AB                                  | 3030                          | 1.4                                            | 0.923                           | 2.797                                          | 75% phosphate cement + 25% CS_B             |
| AP                                  | 2947                          | 1.4                                            | 0.985                           | 2.903                                          | 75% phosphate cement + 25% CS_P             |
| PP                                  | 2785                          | 1.4                                            | 0.971                           | 2.704                                          | 75% Portland cement + 25% CS_P              |
| PB                                  | 2859                          | 1.8                                            | 0.829                           | 2.370                                          | 75% Portland cement + 25% CS_B              |
| IFS/CS_B                            | 2017                          | —                                              | 1.360                           | 2.743                                          | 100% induction furnace slag                 |
| CFA/CS_B                            | 1646                          | 1.3-2.1                                        | 1.200                           | 1.975                                          | 100% coal fly ashes                          |
| CBA/CS_B                            | 2019                          | —                                              | 1.290                           | 2.605                                          | 100% coal bottom clinkers                   |
| CBC/CS_B                            | 1730                          | —                                              | 1.350                           | 2.336                                          | 100% coal bottom clinkers                   |
| ACW/CS_B                            | 3100                          | 1.4                                            | 1.019                           | 3.159                                          | 100% coal bottom clinkers                   |
| IFS/CSA                             | 1741                          | —                                              | 1.270                           | 2.211                                          | 50% IFS + 50% CFA                           |
| CBC/CSA                             | 2054                          | —                                              | 1.280                           | 2.629                                          | 50% CBC + 50% CFA                           |
| IFS/CSA                             | 2054                          | —                                              | 1.280                           | 2.629                                          | 50% IFS + 50% CFA                           |
| RSG (S1–1)                          | 2551                          | 0.8                                            | 0.720                           | 1.836                                          | 100% reduced slag                           |
| RSG (S1–2)                          | 2365                          | 0.7                                            | 0.570                           | 1.348                                          | 93% reduced slag + 5% graphite               |
| RSG (S2–1)                          | 2350                          | 0.5                                            | 0.510                           | 1.198                                          | 50% reduced slag + 5% graphite               |
| RSG (S2–2)                          | 2515                          | 1.0                                            | 1.200                           | 3.018                                          | 48.5% reduced slag + 48.5% clay + 3% graphite|
| RSG (S2–3)                          | 2504                          | 1.30                                           | 0.660                           | 1.652                                          | 47.5% reduced slag + 47.5% clay + 5% graphite|

Where EAF-slag: electric arc furnace slag; CS_P & CS_B: by-product (copper slag) of pyrometallurgical refining process of copper; IB: by-product (mainly sodium chloride) of potash production; WDF: electric arc furnace slag; WRutF: by-product (mostly silica oxide) from ilmenite mining; CBPC_B: phosphate cement/CS_B; CBPC_P: Phosphate cement/CS_P; AB: Aluminous cement/CS_B; AP: Aluminous cement/CS_P; PP: Portland cement/CS_P; PB: Portland cement/CS_B; IFS: induction furnace slag; CFA: coal fly ashes; CBA: coal bottom ashes; CBC: coal bottom clinkers; ACW: asbestos containing waste.
closed to that of CS_P&B (copper slag, 0.8–1.1 W·m⁻¹·K⁻¹) [43]; lower than that of cofalit (1.4–2.0 W·m⁻¹·K⁻¹) [21, 40], electric arc furnace waste (1.3 ~ 2.1 W·m⁻¹·K⁻¹) [22], coal fly ash (1.3–2.1 W·m⁻¹·K⁻¹) [22] and steel slag (2.0 ~ 3.5 W·m⁻¹·K⁻¹) [44].

3.3.2. Storage capacity

Specific heat capacity is an important parameter to characterize the heat storage capacity of materials. The larger the specific heat capacity, the greater the heat storage capacity. Figure 7 shows the logarithm scale of specific heat capacity (Cₚ) derived from DSC results in the high temperature range of 500 °C ~ 1200 °C. The symbol points in the figure are the test results, and the straight line is the fitting curve by using exponential function. The fitting curve is in good agreement with the experimental results. As can be seen from figure 7, the specific heat capacity of the material changes continuously and there is no obvious sudden peak or valley peak, indicating that there is no phase transition during heating. As the temperature increases, the specific heat capacity increases, which is related to the lattice vibration. The heat energy absorbed by the material is stored in the form of phonons or photon kinetic energy. With the increase of temperature, the total kinetic energy of lattice vibration increases with the increase of the number of phonons (or photons) and the enhancement of phonons (or photons) vibration [47]. Therefore, with the increase of temperature, the material stores more heat energy and the specific heat capacity increases.

In S1 series, the Cₚ of S1–1 base sample is 723 ~ 7064 J/(kg·K) in the temperature range of 500 °C ~ 1200 °C. With increase of graphite content, the Cₚ decreases with higher gradient. Generally speaking, the specific heat capacity of solid materials has little effect to do with the structure of the material, but is related to the density of the material [48]. As seen in figure 3, the addition of graphite leads to a decrease in material density, which in turn leads to a decrease in specific heat capacity. For S2 series experiments shown in figure 7(b), the Cₚ of S2–1 sample without graphite generally shows low Cₚ values. When the graphite content is 3%, the Cₚ increase significantly ranging from 1203 to 17608 J/(kg·K), almost twice as much as Cₚ of S1–1 sample. With further increase of graphite
content, it shows decrease tendency. When the graphite content is more than 3%, the specific heat capacity decreases sharply due to the decrease of the density.

Also it can be seen from figure that, $C_p$ values are low at temperature below 600 °C, but it is high at temperature above 600 °C, so it is suitable for the application in the field of high temperature heat storage. The $C_p$ values of RSG(S1–1&81–2) and RSGC(S2–1&8S2–2) together with reported values [25, 45, 46] of similar waste materials at 500 °C are listed in the table 5. As seen in the table, $C_p$ values of studied materials are in the range of reported values available in the literature. $C_p$ of RSG(S1–2) and RSGC(S2–1) samples are low, but $C_p$ of RSGC(S2–2) sample is higher than most of reported data.

Thermal capacity, $\rho \times C_p$ is a critical parameter which dictated the packed bed TES system performances, and determine the energy density of the storage tank [46]. Thermal capacities of the sintered materials at 500 °C are also summarized in table 5. Although the specific heat capacity of sintered material prepared in this study is not high, due to its high density, the thermal capacities are in the range (1.032 ~ 4.760 MJ m$^{-3}$·K) of reported values [21, 25, 45, 46]. Maximum thermal capacity appears on sample RSGC(S2–2) and it is 3.018 MJ m$^{-3}$·K.

3.3.3. Heat storage density
Energy density of storage materials can be defined as energy release per unit volume or unit mass. Higher energy can be stored in materials with higher energy densities [49]. To clarify the storage energy capacity at high operating temperature, heat storage density in temperature range of 500 °C ~ 900 °C is calculated by integrating the specific heat capacity regression function. Figure 8 shows the heat storage density of sintered materials at $\Delta T = 100$ K (500 °C ~ 600 °C), $\Delta T = 200$ K (500 °C ~ 700 °C), $\Delta T = 300$ K (500 °C ~ 800 °C), and $\Delta T = 400$ K (500 °C ~ 900 °C). At a fixed $\Delta T$, the density of heat storage gradually decreases with the increase of graphite content due to decrease of specific heat capacity. In the $\Delta T$ range of 100 ~ 400 K, the heat storage density of S1–1 and S1–2 materials are 89 ~ 633 kg kJ$^{-1}$ and 213 ~ 107 kg kJ$^{-1}$ respectively. With the increase of $\Delta T$, the increasing degree of heat storage density is greater. This actually indicates that graphite is more
effective to the heat storage density in the high temperature range. This behavior can be seen more clearly in the sample S2–2 and S2–3 shown in figure8(b). In the S2 series of experiments, the peak appears near 5% graphite. In the range of $\Delta T = 100 \sim 400$ K, the heat storage densities of S2–2, S2–3, and S2–4 samples are $167 \sim 1221$ kJ kg$^{-1}$, $81 \sim 1961$ kJ kg$^{-1}$, and $105 \sim 828$ kJ kg$^{-1}$ respectively.

Table 6 lists heat storage density, heat storage capacity and mass required to generate 1000 kWh, and volume required for 1000 kWh in the temperature range of 500°C – 750°C. From the data collected in these tables it can assert that the studied materials except S2–1 have similar or even higher performance compared to those reported in the literature [14]. Due to high specific heat capacity, S2–2 specimen has best combination of highest heat storage capacity (0.155 kWh kg$^{-1}$), lowest mass (6442 kg) and volume (m$^3$) required for generating 1000 kWh.

Although the appropriate amount of graphite can obviously improve the material’s heat storage density and heat storage capacity, and reduce the mass or volume needed for heat storage, the excess graphite content leads to the decrease of density, hardness and specific heat capacity, so the graphite content should not be too high. Base on the results in the table 6, it can be known that the graphite content should be controlled in the range of 3 ~ 5%.

Taking into account all the results of thermophysical properties investigated in present study, the RSG (S1–2), RSGC(S2–2) and RSGC(S2–3) materials can be considered as feasible SHS materials applied in the high operating temperature range(500°C ~ 1200°C) of CSP plant.

4. Conclusions

High temperature (>500°C) SHS materials was prepared through the means of carbothermic reduction followed by the sintering method using vanadium tainings as main raw materials, graphite as thermal conductivity modifier and clay as auxiliary materials. The following conclusions could be drawn:

(1) Phase analysis by XRD shows that main phases of sintered material without clay addition include aluminosilicate, sodium aluminoslicate, ilmenite and graphite, while additional phase of quartz and carbonate were observed in the samples with clay addition.

(2) With increase of graphite content in the range of 0 ~ 15%, the both density and hardness of materials without adding clay showed a decreasing tendency, while thermal conductivity gradually increased from 0.54 to 1.54 W·m$^{-1}$·K$^{-1}$.

(3) The density and hardness of sintered materials with clay addition increased first and then decreased, while the thermal conductivity remained constant at first, and then increased from 0.754 to 1.922 W·m$^{-1}$·K$^{-1}$.

(4) The DSC results show that when graphite content is 3 ~ 5%, both sintered materials with and without clay addition show high thermal capacity (>1.2 MJ m$^{-3}$·K) at temperature above 500°C, and high heat storage density (>200 kJ kg$^{-1}$) in the temperature range of 500°C–750°C. The results revealed that SHS material prepared in this study is a potential high temperature SHS material.

| Material         | Energy stored $\Delta T = 25$ 0K (kJ kg$^{-1}$) | Heat storage capacity $\Delta T = 25$0K (kJ kWh kg$^{-1}$) | Mass required for 1000 kWh (kg) | Volume required for 1000 kWh (m$^3$) |
|------------------|-----------------------------------|--------------------------------------------------------|-----------------------------|-----------------------------|
| Alumina          | 200                                 | 0.056                                                   | 18000                      | 4.5                         |
| High Al concrete | 245                                 | 0.068                                                   | 14700                      | 6.1                         |
| Geopolymer       | 298                                 | 0.083                                                   | 12100                      | 5.1                         |
| Graphite         | 178                                 | 0.049                                                   | 20300                      | 9.1                         |
| Magnesium oxide  | 235                                 | 0.065                                                   | 15300                      | 4.3                         |
| Silicon carbide  | 260                                 | 0.072                                                   | 13800                      | 4.3                         |
| ACW              | 256                                 | 0.071                                                   | 14000                      | 4.5                         |
| RSG(S1–1)        | 293                                 | 0.081                                                   | 12278                      | 4.8                         |
| RSG(S1–2)        | 205                                 | 0.057                                                   | 17523                      | 7.4                         |
| RSGC(S2–1)       | 132                                 | 0.037                                                   | 27087                      | 11.5                        |
| RSGC(S2–2)       | 558                                 | 0.155                                                   | 6442                       | 2.6                         |
| RSGC(S2–3)       | 295                                 | 0.082                                                   | 12179                      | 4.9                         |
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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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