ABSTRACT SUMMARY
Encapsulated potassium nitrate was developed for use as a high temperature phase change material in solar thermal energy storage applications. Fluid bed coating was used to apply three separate layers to a potassium nitrate prill for mechanical stability and accommodation of thermal expansion by the salt during its phase change. The capsule is stable above 500 °C and thermal cycling through the 334 °C melting point of the salt was demonstrated.

INTRODUCTION
Encapsulated phase change materials (PCMs) are present in multiple industries for use in textiles, construction materials, consumer products, and printed materials.1-3 Sequestering the PCM within a small sphere increases surface area and heat exchange rate with the surrounding environment, resulting in improved performance for energy storage applications. An additional application that can benefit from the use of encapsulated PCMs is solar thermal energy storage. Concentrated solar power plants use higher temperature phase change materials to transport heat from a light collection system to a heat engine, such as a steam generator. The use of encapsulated PCMs can enable storage of latent heat overnight when solar heat is unavailable.4,5 This abstract summarizes the development of a high temperature encapsulated phase change material.

Molten salts, such as potassium nitrate (KNO₃) or related eutectics are commonly used as solar heat transfer fluids. The phase change from solid to liquid occurs at 334 °C for KNO₃, and the overall solar thermal energy system can often reach 550 °C. Common encapsulation techniques and previously developed encapsulated PCMs are unstable at the solar thermal energy system temperatures, requiring the development of new formulations to survive the high temperatures. Furthermore, inorganic salts expand 10-15% by volume when transitioning from a solid to a liquid. Therefore, an encapsulated PCM with an inorganic salt core must be able to withstand the increase volume with temperature.

A high temperature encapsulated phase change material was designed using a three-shell system. Inner and outer shells were formulated with a montmorillonite clay base, ceramic binder, and organic film former. The clay and binder provide structural and thermal support, while the organic film former aids in application of the inorganic matrix to the surface of the salt bead. The middle layer is composed of a sacrificial organic material, burned out to leave a void within the capsule for expansion of the salt during melting of the core material. An illustration of this encapsulation system is shown in Figure 1.

EXPERIMENTAL METHODS
Fluid bed coating was used to apply three layers onto 2 mm prills of KNO₃. The inner layer was applied from a slurry in ethanol/water to form a coating containing clay, ethyl cellulose, and colloidal alumina. The middle layer of hydroxypropyl methylcellulose was applied from water. The outer layer was a repeat of the inner layer formulation. The final composition was 3-15% of the inner layer, 5-20% of the middle layer, 20-30% of the outer layer, and over 50% KNO₃ core material, by weight.

To remove the sacrificial organic layer and organic film formers, the capsules were heat treated up to 500 °C in air at a rate of 1°C/min. Multiple isotherms were included to control the decomposition rate of the sacrificial layer.

Electron micrographs were captured with a Carl-Zeiss EVO-50EP environmental scanning electron microscope (ESEM). Thermogravimetric analysis and heat flow data were acquired with a TA Instruments Q600.
RESULTS AND DISCUSSION

Microencapsulated KNO$_3$ was successfully prepared using a triple layer shell system applied with a fluid bed coating process. The inner layer separated the HPMC middle layer from the KNO$_3$, preventing rapid oxidation during heat treatment. Thermal treatment up to 310 $^\circ$C removed the sacrificial layer, leaving a void for expansion of the KNO$_3$ after melting above 334 $^\circ$C. The outer layer provided structural support for the capsule, following removal of the sacrificial layer and ethyl cellulose film forming material. The capsule remained intact after heat treatment to 500 $^\circ$C. Figure 2 shows images of the capsules after heat treatment to 500 $^\circ$C, with cross-sections of capsules shown on the right. Upon cooling, the KNO$_3$ deposits on the inside wall of the capsules, shifting the void space from the second layer of the shell system to the core of the capsules.

Figure 2. Optical micrographs of encapsulated KNO$_3$ heated to 500$^\circ$C.

Thermal analysis, shown in Figure 3, confirms that occurrence of a phase change within the capsules as they are cycled from 250 $^\circ$C to 400 $^\circ$C. The blue dotted line indicates the temperature of the sample as it oscillates between 250 $^\circ$C and 400 $^\circ$C with ramp rates of 10 $^\circ$C/min. The red line shows heat flow of the system, with thermal events that correspond to the melting and freezing of the salt. The thermal events do not match the melting point of the salt at 334 $^\circ$C. The melting point is likely altered by contamination of the salt by the decomposing organic material and ion exchange with the sodium montmorillonite clay. Inspection of the capsules after 10 cycles shows no sign of capsule breakdown.

CONCLUSION

A high temperature phase change material was developed, consisting of KNO$_3$ core material and clay-based composite shell material. The capsule was designed to accommodate the high temperatures of solar thermal energy processing, over 500$^\circ$C, and the thermal expansion of the KNO$_3$ core during melting. Future work is underway, focused on optimizing the capsule formulation and demonstrating stability over 5000 heat-cool cycles.

REFERENCES

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