

11 Phase-Change Materials

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Phase-Change-Material Applications

The use of phase-change materials (PCMs) for thermal control is not new; consider the use of the icebox to store perishable foods before the development of efficient, inexpensive, active refrigeration systems. Recently, however, research and development in PCM technology has resulted in novel applications for both terrestrial and space environments.

The numerous electrical components on a spacecraft present thermal-control challenges. High-power-dissipating components must be prevented from overheating, without the earthbound benefits of free convection to the air or conduction to a cold plate. Conversely, components that are only activated occasionally must be prevented from cooling to temperatures below operational level, and the lack of atmosphere precludes normal convective methods of thermal control. Such components present an ideal application for PCM thermal control.

The simplest form of PCM thermal control for electronic components is the one that is used for short-duty-cycle components in launch or reentry vehicles. Although such components are used only once, they generate large quantities of heat that must be removed so that they will not overheat and subsequently fail. A PCM can thermally protect such a component, as shown in Fig. 11.1. The generated heat is absorbed via latent heat of fusion by the PCM without an appreciable temperature rise of the component. This kind of system is totally passive and very reliable.

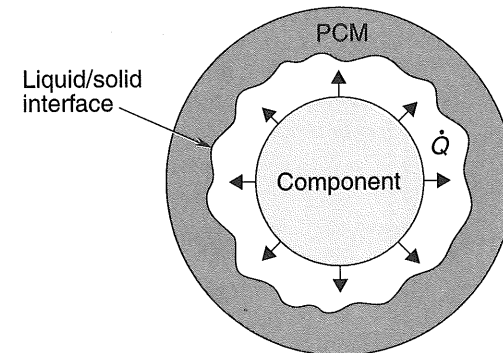


Fig. 11.1. PCM thermal-control system for one-duty-cycle electronic component on launch or reentry vehicle. (Courtesy of NASA^{11.1})

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A more general application of PCM thermal control for electronic components is for cyclically operating components (i.e., ones that operate in on-off cycles). Such a system is shown in Fig. 11.2. In this arrangement, when the component generates heat during the “on” portion of its cycle, the energy is stored via phase change in the PCM. During the “off” portion, the heat-of-fusion energy is removed via radiator, heat pipe, thermal strap, or other means, to refreeze the PCM in preparation for the next “on” portion. The alternate melting and freezing of the PCM enables the component to operate very nearly isothermally at all times.

Three PCM thermal-control systems were used on the Lunar Roving Vehicle (LRV) during the Apollo 15 mission. The first was attached to the Signal Processing Unit (SPU) and to batteries via thermal straps. During each LRV sortie, the heat produced by the SPU was absorbed through phase change in the PCM package. The thermal mass of the batteries offered additional heat-storage capability. After the sorties, louvers were opened on a radiator that was also connected to the PCM package via thermal straps. The PCM was thus refrozen by dumping the latent heat of fusion to space via radiation, thereby preparing the PCM package for the next sortie. The second PCM system was integrally bonded to the Drive Control Electronics (DCE). During a sortie, the heat dissipated within the DCE was absorbed by the PCM. After the sortie, the PCM was refrozen via a thermal-strap louvered radiator system. The third PCM system was integrally bonded to the Lunar Communications Relay Unit (LCRU). During a sortie, heat generated by the LCRU was stored within the PCM. After the sortie, insulation pads covering radiator surfaces on the LCRU were manually removed to allow heat radiation to escape to space, to refreeze the PCM.

This concept of storing and releasing energy via phase change can be extended to a larger scale for space missions that will present varying spacecraft thermal

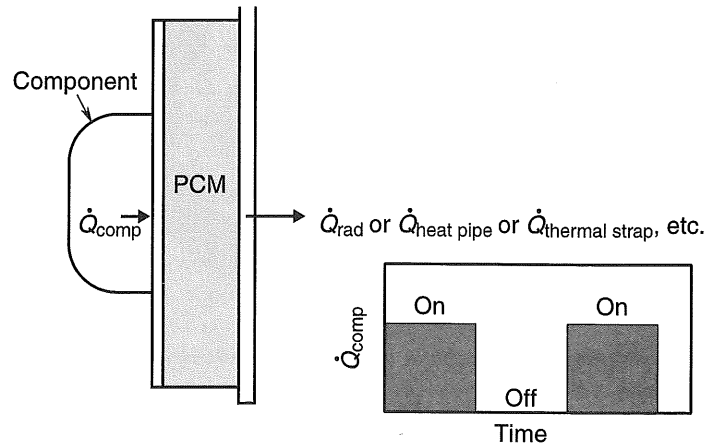


Fig. 11.2. PCM thermal-control system for cyclically operating components. (Courtesy of NASA^{11.1})

environments. For example, a satellite orbiting Earth encounters drastically different thermal environments cyclically as it passes in and out of Earth’s shadow. During such a mission, a PCM package can store and release solar energy to damp the otherwise large temperature changes that a spacecraft would experience during the orbit cycle. This strategy could enable a crew compartment or refrigeration compartment to remain nearly isothermal throughout the orbit. The compartment could be enveloped by a layer of PCM that would absorb and release solar energy during the orbit to provide isothermal conditions at the melting-point temperature of the PCM.

Another example of variable spacecraft thermal environment is encountered by landing vehicles on planets or moons that do not have an atmosphere. The day/night cycle on those bodies presents a thermal environment that changes radically. If the landing craft is enshrouded in PCM, solar energy can be conserved from the day for use during the night, thus ensuring a stable inner thermal environment for crew and/or components.

Another sample PCM thermal-energy storage (TES) device is shown in Fig. 11.3, in schematic form. Energy from electronic components lost through dissipation, which generally is treated as wasted energy, can be heat-piped to a central PCM TES device for later use in thermal control or energy production. This recovery of usually wasted energy for conversion into reusable energy should be beneficial for long space voyages.

PCMs with high melting-point temperatures can be used in conjunction with electronic power-producing systems. Radiators for collecting solar energy can be packed with PCM to store the energy via phase change at the melt temperature. This stored energy can then be converted into electrical power by using the large temperature difference between the radiator and deep space to drive either thermionic or thermoelectric devices. If the power-producing devices are sized for the mean solar power received during the planetary orbit, production of electrical power can continue during the shadow portion of the orbit because of the capability of the PCM to store heat and maintain the radiator at a constant temperature. With conventional photoelectric radiators, the power production ceases during the shadow portion of the orbit, and energy is stored in cells or batteries for use during

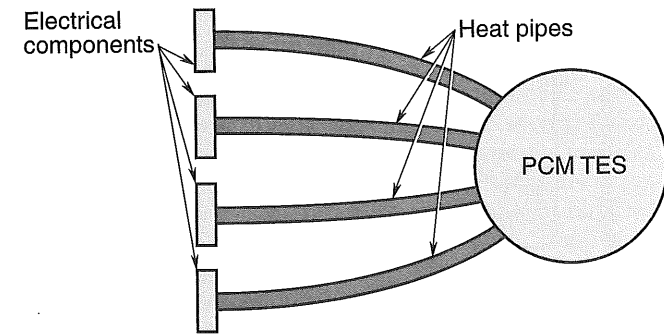


Fig. 11.3. Central PCM thermal-energy storage system. (Courtesy of NASA^{11.1})

the "off" portion of the cycle. When fully developed, the thermionic or thermoelectric concept may offer significant increases in efficiency over the conventional concepts. Preliminary analytical and experimental studies reported by Humphries and Griggs^{11,2} indicate the feasibility of this PCM application, and researchers have identified materials with suitable properties for such PCM systems.

PCM systems can be used in conjunction with space-flight experiments. Many delicate experiments rely upon precisely calibrated instruments. PCM packages can be integrated into these instruments (see Fig. 11.4) to maintain thermal stability or ensure isothermal conditions during the experiment.

PCMs can be used to great advantage in fluid-loop/radiator systems because of their unique isothermal heat-storage capacity. One such application was used on Skylab. The coolant fluid returning from the external radiators experienced sizable temperature variations during the course of an orbit cycle. For efficient operation of the heat exchangers, through which the fluid passed, these temperature variations were too large. A thermal capacitor utilizing PCM damped these temperature variations by alternate melting and freezing, as illustrated in Fig. 11.5. Thus the thermal capacitor maintained the fluid entering the heat exchanger within an allowable temperature range.

Another thermal capacitance application for PCM is in the radiator itself. Ordinarily, if a radiator is to be subject to cyclical heat-removal requirements during a mission, it must be sized for the peak load for successful operation. If PCM is integrated into the radiator, the radiator can be sized for the mean heat-removal requirement, since it can store the energy at peak load via phase change for later

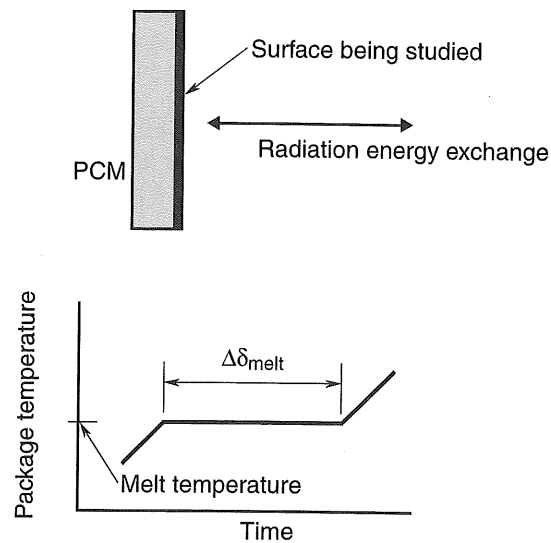


Fig. 11.4. PCM storage for radiometric property device. (Courtesy of NASA^{11,1})

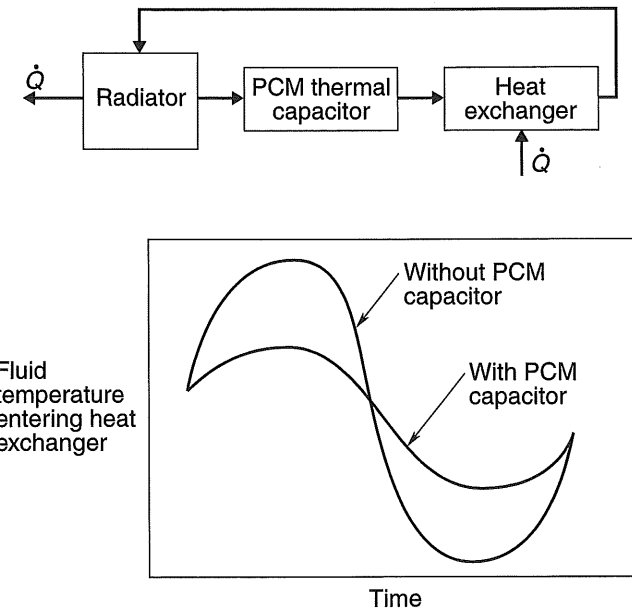


Fig. 11.5. PCM thermal capacitor in fluid loop. (Courtesy of NASA^{11,1})

dumping to space by radiation. Significant savings in area and mass can be obtained with such a PCM radiator.

Phase-Change Materials

The most common phase-change transformations are solid-liquid (melting and freezing), liquid-to-gas (vaporization), solid-to-gas (sublimation), and anhydrous salt transformations. Because of the very large volumetric changes involved in vaporization and sublimation, consideration of these two phase-change transformations for reversible heat storage is impractical. One could, however, design a device, such as a heat pipe, that would act as a reversible heat-storage unit. Usually vaporization and sublimation are used in an open-loop fashion, where the vaporized or sublimed vapor is vented overboard (expendable cooler). Water is a very effective expendable coolant and has been used in several space applications, including Gemini, Apollo, and the space shuttle. Water melts at 0°C, absorbing 333 kJ/kg. The amount of heat required to raise the temperature of water from 0°C to 100°C (sensible heat) is 418 kJ/kg. The amount of heat required to vaporize water at 1 atm of pressure is 2253 kJ/kg. The total energy required to vaporize ice is the sum of the sensible and phase-change heats involved, which is 3004 kJ/kg. Most other expendable coolants absorb considerably less heat, ammonia (NH₃) being the second-best expendable coolant that is used extensively. The design and fabrication of expendable cooling devices for aerospace and military uses is a specialized field.

A number of classes of materials have been investigated for use in phase-change devices. Some of the more important are:

- inorganic salt hydrates, e.g., $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (Glauber's salt) and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
- organic compounds, e.g., paraffins ($\text{C}_n\text{H}_{2n+2}$), alcohols, phenols, aldehydes, and organic acids
- eutectics of organic materials, e.g., 88-mole% acetic acid + 12-mole% benzoic acid
- natural inorganic elements, e.g., sulphur (S).

Table 11.1 gives a representative list of candidate PCMs in the temperature range of -25 to $+62^\circ\text{C}$; the melting-point temperature of most materials listed is

Table 11.1. Typical PCMs in the Range of -25 to $+62^\circ\text{C}$

Material	Melting Point ($^\circ\text{C}$)	Heat of Fusion (kJ/kg)
<i>n</i> -Eicosane ($\text{C}_{20}\text{H}_{42}$)	37	246
Polyethylene glycol 600 [$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$]	20–25	146
Nitrogen pentoxide (N_2O_5)	30	320
Phosphonium chloride (PH_4Cl)	28	752
Dibasic sodium phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$)	37	279
Sodium sulfate ($\text{Na}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$)	31	215
Glycerol [$\text{C}_3\text{H}_5(\text{OH})_2$]	18	199
Calcium chloride ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$)	29	170
<i>p</i> -Xylene [$\text{C}_6\text{H}_4(\text{CH}_3)_2$]	16	164
Sodium chromate ($\text{Na}_2\text{CrO}_4 \cdot \text{H}_2\text{O}$)	23	164
<i>n</i> -Undecane ($\text{C}_{11}\text{H}_{24}$)	-25	141
<i>n</i> -Dodecane ($\text{C}_{12}\text{H}_{26}$)	-12	211
<i>n</i> -Tridecane ($\text{C}_{13}\text{H}_{28}$)	-6	155
<i>n</i> -Tetradecane ($\text{C}_{14}\text{H}_{30}$)	6	228
<i>n</i> -Hexadecane ($\text{C}_{16}\text{H}_{34}$)	17	237
<i>n</i> -Heptadecane ($\text{C}_{17}\text{H}_{36}$)	22	213
<i>n</i> -Octadecane ($\text{C}_{18}\text{H}_{38}$)	28	244
<i>n</i> -Nonadecane ($\text{C}_{19}\text{H}_{40}$)	32	187
<i>n</i> -Octacosane ($\text{C}_{28}\text{H}_{58}$)	62	253
1-Tetradecanol [$\text{CH}_3(\text{CH}_2)_{12} \cdot (\text{CH}_2)\text{OH}$]	38	230
Acetic acid (CH_3COOH)	17	187
Water	0	333

near room temperature. This temperature range is pertinent to temperature control of electronic equipment and to environmental control of crewed spacecraft.

Table 11.2 gives a representative list of candidate PCMs for lower-temperature applications, such as infrared detectors and other solid-state electronic devices. Modern material databases can quickly provide lists of several candidate organic or inorganic PCMs for any given melting-temperature range. Keville,^{11.3} Bledjian *et al.*,^{11.4} and Grodzka^{11.5} provide information useful for preparing and conducting a PCM heat-storage development program.

Solid Heat Sinks

Thermal-energy storage may also be accomplished with solid materials. For sensible heat storage the figure of merit is the specific heat of the material, c_p (kJ/kg $^\circ\text{C}$), when weight is critical, or the product of density and specific heat, ρc_p (kJ/cm³ $^\circ\text{C}$), when volume is critical. To avoid large and objectionable temperature

Table 11.2. Typical PCMs for Lower Temperatures

Material	Melting Point ($^\circ\text{C}$)	Heat of Fusion (kJ/kg)
Methyl propyl ketone ($\text{C}_5\text{H}_{10}\text{O}$)	-78	104
Amyl alcohol ($\text{C}_5\text{H}_{12}\text{O}$)	-79	112
1-Methyl-1,2 ethylbenzene (C_9H_{12})	-81	88
Ethyl acetate ($\text{C}_4\text{H}_8\text{O}_2$)	-82	118
Methyl ethyl ketone ($\text{C}_4\text{H}_8\text{O}$)	-86	111
<i>n</i> -Butylbenzene ($\text{C}_{10}\text{H}_{14}$)	-89	82
Isopropyl alcohol ($\text{C}_3\text{H}_8\text{O}$)	-89	88
Butyl alcohol ($\text{C}_4\text{H}_{10}\text{O}$)	-89	125
<i>n</i> -Heptane (C_7H_{16})	-91	140
Toluene (C_7H_8)	-94	72
Ethyl benzene (C_8H_{10})	-95	86
<i>n</i> -Hexane (C_6H_{14})	-95	151
Isopropylbenzene (C_9H_{12})	-96	81
<i>n</i> -propylcyclopentane (C_8H_{16})	-117	88
1-Neptune (C_7H_{14})	-119	126
2,4-Dimethyl pentane (C_7H_{16})	-119	67
Chloropropane ($\text{C}_3\text{H}_7\text{Cl}$)	-123	84
Butane (C_4H_{10})	-135	76
Ethane (C_2H_6)	-172	93
Methane (CH_4)	-183	59

gradients, a heat sink should have a relatively high thermal conductivity. Some of the best-known heat-sink materials for spacecraft applications are beryllium and its alloys, with $c_p = 1.88 \text{ kJ/kg}\cdot^\circ\text{C}$ and $\rho c_p = 0.0035 \text{ kJ/cm}^3\cdot^\circ\text{C}$. Typical aluminum and magnesium alloys, used often in spacecraft designs, have $c_p = 0.837 \text{ kJ/kg}\cdot^\circ\text{C}$ and $\rho c_p = .0019$ to approximately $.0023 \text{ kJ/cm}^3\cdot^\circ\text{C}$. Beryllia and alumina ceramics have been used as sensible heat-storage materials for electronic parts. Sensible heat storage is a well-documented engineering concept, and many handbooks provide values of density, specific heat, and thermal conductivity. At very low temperatures (less than 30 K), the specific heat of most solid materials becomes very low; thus lead and its alloys have been used for heat storage at low temperatures.

When To Use a PCM

As mentioned earlier, PCMs are generally useful for providing stable temperatures or for allowing radiators to be sized for average, rather than peak, heat-load conditions. In either case, the PCM is one of several potential thermal-design approaches. In most spacecraft applications, criteria for design selection boil down to which one has the lowest mass and power requirements, with further programmatic factors such as cost and development complexity also playing substantial roles. Competing thermal-control approaches include using a solid heat sink made from a high-specific-heat material such as beryllium, relaxing temperature-stability requirements, and using a conventional radiator/heater system. In the trade-off with a solid heat sink, an efficiently packaged PCM will usually show a mass advantage over the solid heat sink, but the cost and complexity of developing the PCM design may make it unattractive to the program if the mass savings are not substantial. For designs where the goal is to reduce temperature cycle ranges, the trade between temperature stability and thermal-design mass and cost must also be made on a case-by-case basis according to the value system of the particular program.

A direct comparison of the mass for a PCM radiator design with mass for a non-PCM design can be made, because the PCM design is not affected by subjective programmatic values. For a given application, we can safely say that the radiator size and mass may be reduced through the use of thermal storage if the peak heat-dissipation rate is larger than the average heat-dissipation rate. The first question that the thermal engineer must answer, however, is whether the added mass of the thermal-storage system is less than the mass saved by reducing the radiator size, i.e., is there a net benefit? With launch costs sometimes exceeding \$20,000/kg, a substantial mass savings could pay any additional development cost for the PCM system. In some cases, a spacecraft program may have to reduce mass to meet launch vehicle mass limits, making any mass savings even more valuable.

The first step in the trade-off is to bound the limits of thermal-storage benefits by determining the maximum potential mass savings of a thermal system with a PCM versus one without. To control a payload component to its desired temperature requires sizing the radiator for peak dissipation if thermal storage is not considered and somewhere between the peak and average dissipation if thermal storage is included. A bound can be derived for the benefit of thermal storage if we

compare the peak-power-sized thermal system mass with the average-power-sized system mass including storage.

Busby and Mertesdorf^{11.6} have outlined an analytical technique to identify the duty cycle at which a PCM becomes attractive in a design. Using their approach, consider the general case of a payload having a periodic heat dissipation pulse of magnitude \dot{Q}_{pulse} and a duty cycle of β , as shown in Fig. 11.6. (The duty cycle is the fraction of the total cycle time, Δt_{cycle} , that the payload is "on.") If we use a radiator weighing m_{rad} kg/m² that can reject a net \dot{Q}_{rad} W/m² and a PCM system that can store Q_{PCM} W·hr/kg (including the mass of packaging), we can calculate the masses of the competing systems as

$M_{\text{w/oPCM}}$ = mass of radiator sized for peak component dissipation rate.

$$M_{\text{w/oPCM}} = \frac{(\dot{Q}_{\text{pulse}} m_{\text{rad}})}{\dot{Q}_{\text{rad}}} \quad (11.1)$$

$M_{\text{w/PCM}}$ = mass of radiator sized for average heat rate plus weight of PCM system.

$$M_{\text{w/PCM}} = \frac{\beta (\dot{Q}_{\text{pulse}} m_{\text{rad}})}{\dot{Q}_{\text{rad}}} + \frac{\beta \Delta t_{\text{cycle}} (\dot{Q}_{\text{pulse}} - \beta \dot{Q}_{\text{pulse}})}{Q_{\text{PCM}}} \quad (11.2)$$

Setting these two equations equal to one another, we can solve for the heat-pulse duty cycle, β' , at which the PCM design becomes attractive from a mass perspective (Ref. 11.33):

$$\beta' = \frac{m_{\text{rad}} Q_{\text{PCM}}}{\dot{Q}_{\text{rad}} \Delta t_{\text{cycle}}} \quad (11.3)$$

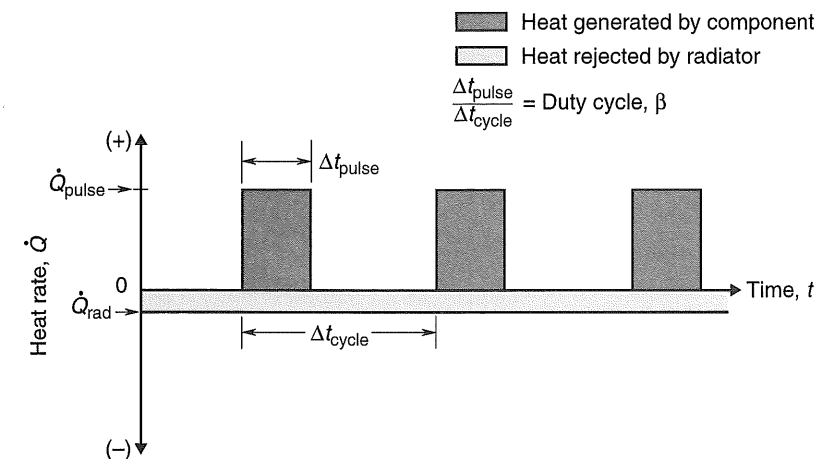


Fig. 11.6. Periodically operating component.

This equation clearly shows that the physical constants describing the characteristics of the thermal system set an upper bound on the maximum pulse duration for which thermal storage makes sense. Duty cycles greater than β' do not benefit from thermal storage because the mass penalty associated with the PCM and its packaging is greater than the mass saved as the result of using a smaller radiator.

This upper limit for the usefulness of thermal storage is illustrated by the example shown in Fig. 11.7, in which the masses of designs with and without PCMs are shown as a function of component heat-pulse duration. This example assumes a component dissipating 1000 W for a portion of the 1.5-hour orbital period is mounted to a wall of a spacecraft that can be used as a radiator surface. Because an existing structural panel is used, radiator mass is assumed to be limited to the mass of the heat pipes needed to spread the heat from the component plus the mass of thermal surface finishes, or about 5 kg/m^2 . Furthermore, the radiator is assumed to be capable of rejecting a net 300 W/m^2 to the external environment and a PCM with high-performance packaging is assumed to be available to give a net specific storage capacity of 35 W-hr/kg . As can be seen in Fig. 11.7, PCMs show a net advantage for a pulse duration less than 35 min for a 39% duty cycle in this particular application. The results of this calculation are, of course, highly dependent on the parameters assumed, and the critical duty cycle will vary from application to application. In the case of very small duty cycles, the mass of the equipment being cooled (which was not included in the preceding example) may be large enough to directly absorb the heat pulse with an acceptably small rise in temperature, making a PCM unnecessary. In other cases, benefits such as heater power reduction or smaller heat-transport loops to connect the component to a remote radiator may also need to be considered. In such cases, the above preliminary assessment approach would still apply but would require modification to account for any mass savings in the power subsystem or heat-transport loop.

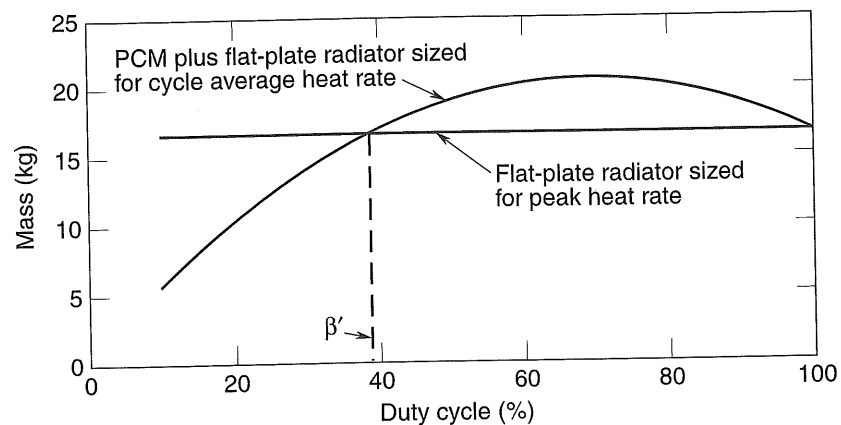


Fig. 11.7. Thermal-control mass with and without PCM.

PCM Design Details

In designing PCM thermal-control systems for specific applications, a number of factors other than heat of fusion must be considered. These include thermodynamics, heat transfer, combined thermodynamics and heat transfer, the function of fillers, containment, and an engineering approach that yields the proper design of a PCM thermal-control system from the initial requirements. The design guidelines presented in this section were developed during a study conducted by Lockheed (now Lockheed Martin) for NASA's Marshall Space Flight Center in 1971.^{11.1}

Choice of PCM

In selection of a PCM for a specific application, the most important criterion is the operational temperature range of the component to be protected. The PCM must have a melting-point temperature well within this range to ensure that unintentional undercooling or overheating will not damage the component. Tables 11.1 and 11.2 give the melting-point temperatures of some representative PCMs, and extensive data on these and many others can be found in Humphries and Griggs^{11.2} and Hale and Hoover.^{11.1}

Designing and fabricating thermal-storage devices for solid-liquid transformation is considerably simpler than selecting a PCM because of the absence of a large volumetric change in melting or freezing. The selection of a suitable PCM, however, is often a project of considerable size and complexity. A good PCM should possess the following characteristics: high heat of fusion per unit mass; proper melting-point temperature (or temperature range); noncorrosiveness; non-toxicity; reversible solid-to-liquid transition; high flash point; low coefficient of expansion; stability; high thermal conductivity in both phases; little or no supercooling; and low vapor pressure at room temperature. A realistic figure of merit should take all these desirable characteristics into consideration. One should not assume that once a good match on melting-point temperature is found, high heat of fusion per unit mass is the controlling characteristic. However, an effort should be made to select a PCM with a heat of fusion greater than 150 kJ/kg for room-temperature applications, and greater than 40 kJ/kg for cryogenic applications.

If more than one PCM is found with suitable melting-point temperatures, comparisons of other characteristics should be made to eliminate all but the best PCM. The secondary characteristics that should be considered are summarized in Table 11.3. None of the PCM candidates may be superior in all characteristics, so engineering trade-offs may be necessary in selecting the best PCM for a specific application. In general, the prime candidates should cause fewer design problems than their nonprime counterparts.

Thermodynamic Considerations

To design a PCM thermal-control system properly, the analyst generates thermodynamic conservation equations for the system. These simple thermodynamic relationships allow estimation of the energy-storage requirements of the PCM, the required mass of PCM, and the size of the radiator. While these relationships will vary from application to application, the following example illustrates the general method for quantifying the thermodynamic relations for a specific application.

Table 11.3. Secondary Characteristics of PCMs

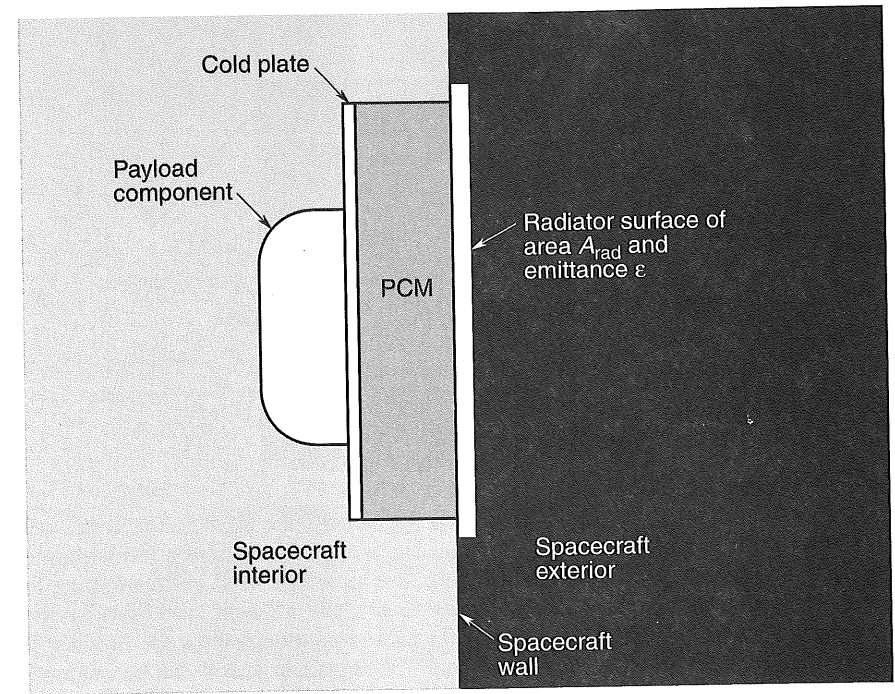
Property or Characteristic	Desirable Value or Tendency
Heat of fusion	High
Thermal conductivity	High
Specific heat	High
Density	High
Volume change during melting	Low
Vapor pressure	Low
Melting and freezing behavior	Dependable and reversible
Availability	Readily available
Cost	Low
Compatibility	Compatible with container and filler materials
Toxicity	Nontoxic
Hazardous behavior	Not exhibited
Property data	Readily available and well documented
Surface tension	Low

Consider a component with the cyclical heat-generation profile shown in Fig. 11.6. Its temperature is to be controlled by the PCM package/radiator system in Fig. 11.8. Since the component is to be controlled to a specific temperature, the ideal radiator will operate very close to the PCM melting-point temperature at all times and have nearly constant radiant-heat rejection to the external environment. If the component heat generation and radiation to space are the only energy exchanges to which the package is subject, the radiator is sized so the total energy dissipated by the component during one cycle equals the total energy radiated by the radiator over that same time period. This is expressed mathematically as

$$\epsilon A_{\text{rad}} \sigma T_{\text{melt}}^4 \Delta t_{\text{cycle}} = \dot{Q}_{\text{pulse}} \Delta t_{\text{pulse}}, \quad (11.4)$$

assuming an absolute-zero thermal-radiation sink and no solar or planetary radiation incident upon the radiator surface. (For applications in which incident radiation is appreciable, the above equation must be adjusted by subtracting the radiant energy absorbed from the surroundings from the energy emitted by the radiator.) Since T_{melt} , ϵ , Δt_{cycle} , \dot{Q}_{pulse} , and Δt_{pulse} are fixed quantities for any particular application, the required radiator size may be calculated as follows:

$$A_{\text{rad}} = \frac{\dot{Q}_{\text{pulse}} \Delta t_{\text{pulse}}}{\sigma \epsilon T_{\text{melt}}^4 \Delta t_{\text{cycle}}} = \dot{Q}_{\text{gen,avg}} \left(\frac{1}{\sigma \epsilon T_{\text{melt}}^4} \right) \quad (11.5)$$

**Fig. 11.8. PCM/radiator thermal-control system.**

Notice that the PCM allows the radiator to be sized for the average power being dissipated by the component over the entire cycle. If a PCM were not used, the radiator would have to be sized for the peak heat rate encountered during the pulse, making such a radiator larger by the ratio $\dot{Q}_{\text{pulse}}/\dot{Q}_{\text{avg}}$. Reduction of radiator size and mass is therefore one of the advantages of a PCM system.

The net energy stored in the PCM as the component goes through its on/off cycles is shown as a function of time in Fig. 11.9. To store and release the \dot{Q}_{pulse} energy as heat of fusion, the quantity of PCM must be:

$$m_{\text{PCM}} = \frac{E_{\text{max}}}{h_f} \quad (11.6)$$

where E_{max} is as shown in Fig. 11.9.

Heat-Transfer Considerations

Although the thermodynamic considerations are simple and straightforward, the heat-transfer problems are perhaps the largest obstacles in the design of PCM systems. As a general rule, materials with relatively large heats of fusion have relatively low thermal conductivities. Therefore, for significant heat fluxes, a very large temperature difference may be required to transfer the heat from component to PCM. This temperature gradient can result in a large temperature rise of the component during the melting process.

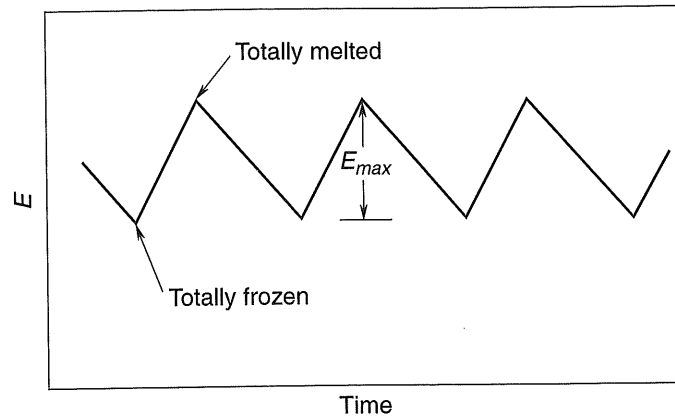


Fig. 11.9. Net energy in PCM.

In the PCM/radiator example discussed previously, the heat fluxes at the cold plate and radiator can be used to determine the temperature distribution within the package as a function of time. An assumption that will be used in determining the temperature distributions is that the time to achieve a linear quasi-steady-state temperature distribution will be shorter than the time required for the liquid/solid interface to move an appreciable distance. The transient period can be neglected principally because c_p/h_f is such a small ratio that the transient period is negligible compared to the time required for appreciable interface movement. The validity of this assumption has been confirmed by computer thermal analysis of representative PCM systems. (Deviations from this assumption would actually result in improved performance, making this a conservative analytical approach.)

At the point during the cycle when total solidification has just occurred, all the heat stored in the PCM will have been rejected to space by the radiator, the surface temperature of which is slightly below the melt temperature of the PCM. The temperature distribution through the system will therefore be as shown in Fig. 11.10.

If the quantity of PCM has been chosen correctly, heat will be conducted from the PCM to the radiator at a constant rate throughout the cycle. Therefore, the slope of the temperature distribution through the PCM's solid portion must equal:

$$\left(\frac{\partial T}{\partial X}\right)_s = \frac{\sigma A_{\text{rad}} \epsilon T_{\text{melt}}^4}{k_s A_{cp}} \quad (11.7)$$

If the thermal-control system has been properly designed, the next component heat pulse should start just as the solid boundary reaches the cold plate and the PCM near the component should begin to melt. After approximately 50% of the PCM has melted, the temperature distribution will be as shown in Fig. 11.11. The slope of the temperature distribution in the solid region remains the same as before, but the liquid phase now has a linear temperature distribution with the slope, and the rate of melting can be easily calculated as

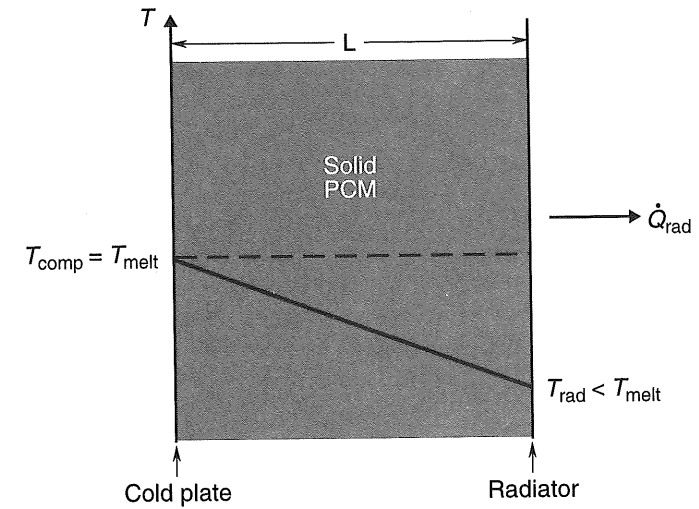


Fig. 11.10. Temperature distribution at total solidification.

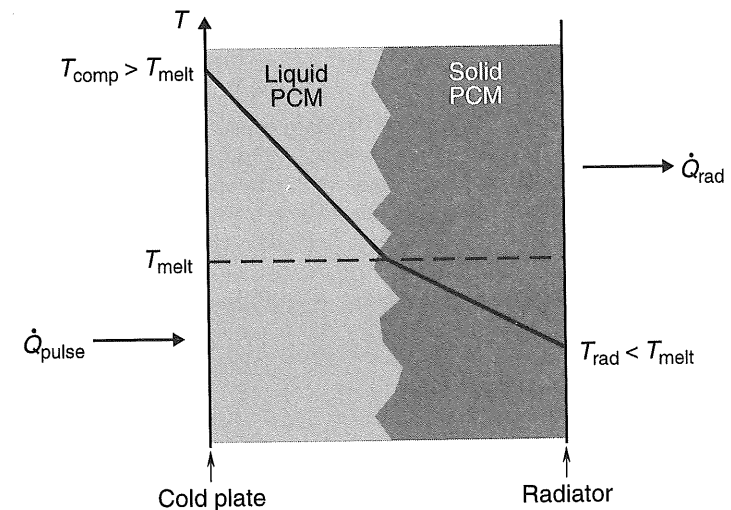


Fig. 11.11. Temperature distribution at 50% melt.

$$\left(\frac{\partial T}{\partial X}\right)_l = \frac{\dot{Q}_{\text{pulse}}}{k_l A_{cp}} \quad (11.8)$$

$$\dot{m} = \frac{\dot{Q}_{\text{pulse}} - \dot{Q}_{\text{rad}}}{h_f} \quad (11.9)$$

When all of the PCM has melted, the distribution will assume the shape shown in Fig. 11.12, and the slope remains the value cited in Eq. (11.7).

Because the liquid phase thickness is maximum at total melt, the component temperature will be at its maximum value at this point, namely,

$$T_{\text{comp}_{\text{max}}} = T_{\text{melt}} + (L) \left(\frac{\partial T}{\partial X} \right)_l \quad (11.1)$$

If the system is optimally designed, the component heat generation will cease just as the liquid boundary reaches the radiator. Freezing will begin at the radiator surface, and the freeze boundary will move toward the cold plate. After 50% of the PCM has frozen, temperature distribution will assume the shape in Fig. 11.13.

The liquid will be near the melt temperature, and the solid will have the slope $(\partial T / \partial X)_s$ described earlier. After the solidification has completed, the distribution will return to that given in Fig. 11.10 and the cycle will then repeat itself.

Of primary importance to the design engineer is the maximum temperature the component will reach during the cycle. Recall the relation developed previously,

$$T_{\text{comp}_{\text{max}}} = T_{\text{melt}} + (L) \left(\frac{\partial T}{\partial X} \right)_l \quad (11.10)$$

$$\left(\frac{\partial T}{\partial X} \right)_l = \frac{\dot{Q}_{\text{pulse}}}{k_l A_{cp}} \quad (11.11)$$

where substitution yields:

$$T_{\text{comp}_{\text{max}}} = T_{\text{melt}} + \frac{\dot{Q}_{\text{pulse}} L}{k_l A_{cp}} \quad (11.12)$$

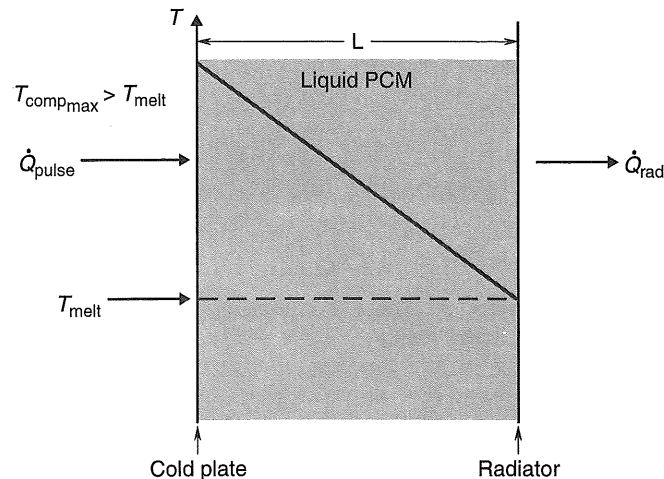


Fig. 11.12. Temperature distribution at total melt.

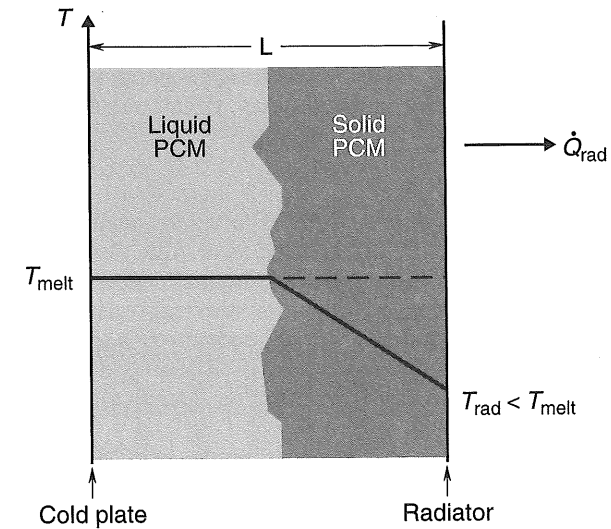


Fig. 11.13. Temperature distribution at 50% solidification.

$$T_{\text{comp}_{\text{max}}} = T_{\text{melt}} + \frac{\dot{Q}_{\text{pulse}} L}{k_l A_{cp}} \quad (11.13)$$

If the component is to operate properly, this $T_{\text{comp}_{\text{max}}}$ must be less than the maximum allowable operating temperature of the component. However, if the best PCM for this operational temperature range has a relatively low thermal conductivity (as is usually the case), the following design barrier presents itself. From the thermodynamic discussions presented earlier,

$$m_{\text{PCM}} = \frac{E_{\text{max}}}{h_f} = \rho_{\text{PCM}} A_{cp} L \quad (11.14)$$

Solving for L yields:

$$L = \frac{E_{\text{max}}}{h_f \rho_{\text{PCM}} A_{cp}} \quad (11.15)$$

Substituting for t in our relation for $T_{\text{comp}_{\text{max}}}$ yields:

$$T_{\text{comp}_{\text{max}}} = T_{\text{melt}} + \frac{\dot{Q}_{\text{pulse}} E_{\text{max}}}{k_l A_{cp}^2 h_f \rho_{\text{PCM}}} \quad (11.16)$$

For a given application and given PCM for the desired temperature range, T_{melt} , Q_{pulse} , E_{max} , k_b , A_{cp} , h_f , ρ_{PCM} are all fixed quantities. Therefore, $T_{\text{comp,max}}$ is fixed, and if it exceeds the maximum allowable operating temperature of the component, it presents an apparent roadblock to the designer. High-conductivity filler materials allow the designer to overcome this obstacle.

The Function of Fillers

When the component temperature rise for a particular application exceeds the maximum operational temperature of the component, filler materials must be integrated into the PCM package to improve the thermal conductivity of the PCM. The function of filler materials is to provide low-thermal-resistance paths through the PCM, thus raising its equivalent thermal conductivity and reducing the temperature gradient necessary to transfer the imposed heat load into the PCM. The reduced temperature gradient thereby reduces the maximum temperature of the component.

A number of different fillers have been tested for use in PCMs, including carbon fibers, copper foam, alumina foam and powder, and aluminum powder, foam, honeycomb, and fins. Aluminum or alumina powder-PCM composites were found to produce no noticeable improvement in the thermal conductivity of lithium nitrate according to Grodzka.^{11.7} Aluminum wool has been found to produce some improvement in system performance, but significantly less than that predicted by the pretest analysis.^{11.8} The same was generally true of the copper and aluminum foams tested. Various test results reported with different PCMs indicate that aluminum honeycomb, aluminum fins, and carbon fibers offer the most system improvement.^{11.7-11.9}

Combined Thermodynamic and Heat-Transfer Relations

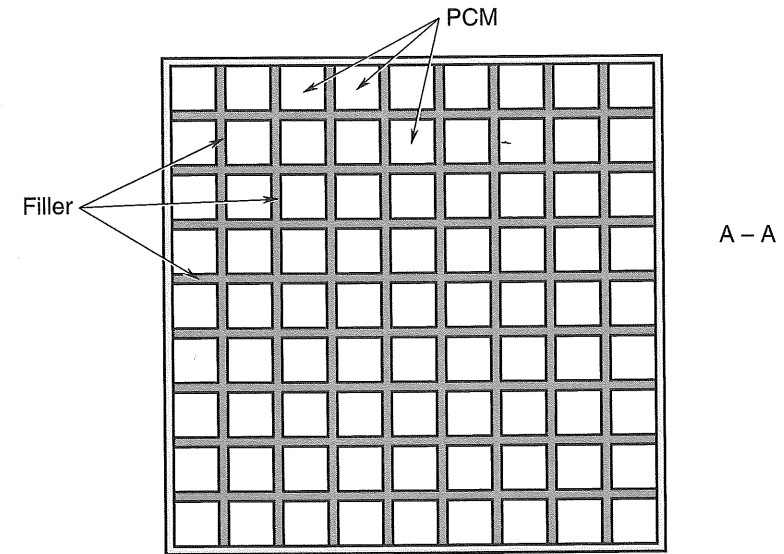
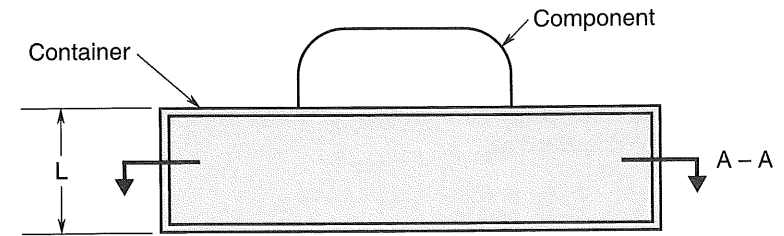
This section is devoted to the development of the combined thermodynamic and heat-transfer relations for a PCM package with filler materials uniformly distributed within. For the purposes of this discussion, we assume that the contact resistance between the filler material and the cold plate is negligible, and that three-dimensional heat-transfer effects between the filler and PCM can be neglected. (The errors introduced by these assumptions are discussed later.)

A conceptual illustration of a PCM thermal-control system using filler materials is shown in Fig. 11.14. Five equations in five unknowns can be derived to describe such a system. These equations represent conservation of energy and mass, additive conductance and area relations, and temperature-range constraints.

Conservation of Energy

After the maximum energy that must be stored by the PCM package E_{max} is determined, the heat balance shown in Eq. (11.17) will hold. This equation includes both the energy stored through latent heat of fusion and sensible heat stored within the liquid PCM and the filler material.

$$E_{\text{max}} = \rho_{\text{PCM}} A_{\text{PCM}} L h_f + \left[\rho_F A_F C_{p_F} + \rho_{\text{PCM}} A_{\text{PCM}} C_{p_{\text{PCM}}} \right] \frac{L}{2} (T_{\text{comp,max}} - T_{\text{melt}}) \quad (11.17)$$



Filler cross-sectional area = A_F
 PCM cross-sectional area = A_{PCM}
 $A_F + A_{\text{PCM}} = A_T = \text{total cross-sectional area}$

Fig. 11.14. PCM package with filler.

(Note: $E = 0$ when filler and PCM are at T_{melt} throughout, and PCM is solid throughout.)

Temperature Range Constraint

As discussed earlier, any resistance in the heat-transfer path between the component and the PCM will cause the component temperature to rise above the PCM melt temperature. This temperature rise must be limited so that the component does not exceed its maximum allowable operating temperature. This constraint may be expressed as

$$\dot{Q}_{\text{pulse}} = \frac{k_T A_T (T_{\text{comp,max}} - T_{\text{melt}})}{L} \quad (11.18)$$

This equation establishes a relation between the total conductivity, area, thickness, and temperature rise of the component, $(T_{\text{comp_max}} - T_{\text{melt}})$.

Additive Conductance Relation

For parallel conductance paths through the PCM and filler, the total equivalent conductance can be described as:

$$k_T A_T = K_{\text{PCM}} A_{\text{PCM}} + k_F A_F \quad (11.19)$$

This relation neglects three-dimensional effects and contact resistances. (The errors imposed by neglecting these factors are discussed later.)

Conservation of Mass

The design engineer will want to know the mass of the PCM, container, and filler. The mass balance shown in Eq. (11.20) will hold.

$$W_T = (\rho_{\text{PCM}} A_{\text{PCM}} + \rho_F A_F) L + \rho_c [2A_T + (4\sqrt{A_T})L] L_C \quad (11.20)$$

The radiator mass is neglected here because the outer surface of the container could be coated to serve as a radiator or another method of heat removal might be used for other applications. Neglecting the thermal mass of the radiator is conservative.

Additive Area Relation

The total area is the sum of the cross-sectional areas of the PCM and filler. Thus,

$$A_{\text{PCM}} + A_F = A_T \quad (11.21)$$

Solution of Simultaneous Equations

For a given application, PCM, filler material, and container material, these five simultaneous equations can be solved to yield W_T , L , k_T , A_{PCM} , and $\Delta T_{\text{excursion}} = T_{\text{comp_max}} - T_{\text{melt}}$ as functions of filler area, A_F . By conducting a parametric study, the thermal engineer can gain insight into the functional relationships between these variables that will lead to an optimal design solution.

As an example, consider a component that dissipates 100 W for 1 h and is mounted on a 0.093-m^2 (1 ft^2) PCM heat sink that uses aluminum as the container and filler material and a fictitious PCM having the properties shown in Table 11.4.

Using the above equations, we can calculate the total mass and thickness of the PCM heat sink and the temperature rise of the component as a function of filler area-fraction, as shown in Fig. 11.15. These curves illustrate several interesting

Table 11.4. Properties of a Fictitious PCM

Property	Variable	Value
Density	ρ_{PCM}	1602 kg/m ³
Thermal conductivity	K_{PCM}	0.519 W/m-K
Specific heat	C_{pPCM}	1673.6 J/kg-K
Heat of fusion	h_f	232,400 J/kg

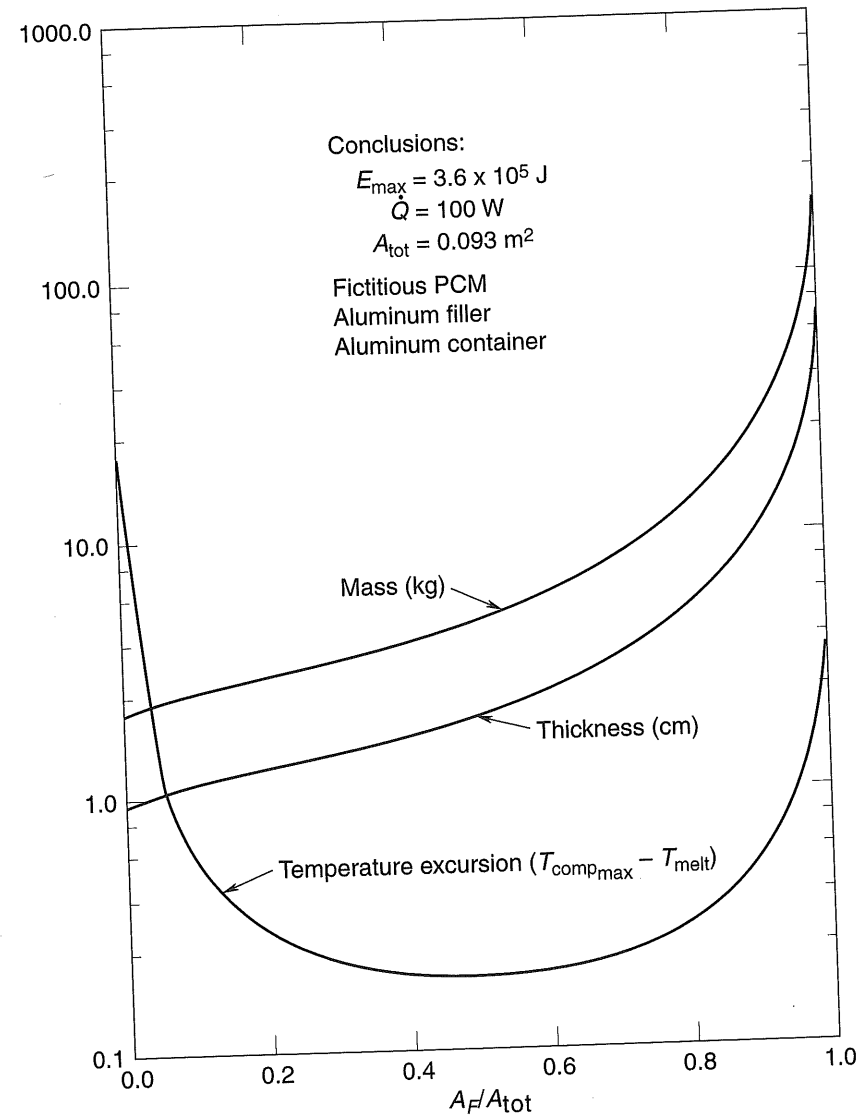


Fig. 11.15. PCM design optimization.

facts. The intersections of the three curves with the y-axis represent the mass, thickness, and temperature excursion for a PCM package without filler. The thickness and mass are least for this condition, and addition of filler causes an increase in both quantities. However, the component temperature rise is highest at this condition, and it decreases drastically with small additions of filler until a minimum point is reached at around 50% filler fraction. The minimum temperature will

occur at the 50% point whenever the sensible heat storage of the package and the thermal conductivity of the PCM have negligible effects upon total energy storage and total heat transfer, respectively. Since most designs will try to maximize the effectiveness of the PCM, the minimum temperature will tend to occur near this 0.5 A_T point. However, for applications in which sensible heat storage and/or PCM thermal conductivity become significant, the minimum value may occur at some other filler fraction. Similarly, the intersections of the three curves with the $A_F/A_{tot} = 1.0$ vertical line represent the mass, thickness, and temperature excursion for a solid aluminum heat sink. At this condition, the mass and thickness reach their maximum values, showing the inferiority of a solid heat sink compared to a PCM package.

Curves of this type can easily be generated for a particular application, PCM, container, filler, and cold-plate area. Knowing the maximum temperature excursion the component can sustain, the designer can consult the curve for temperature excursion and find the minimum filler area required to maintain the excursion below the maximum. From the other curves, the required minimum mass and thickness can be obtained. If the mass represents a savings over other thermal-control techniques, then more sophisticated analytical and experimental design studies should be considered. If either the mass or the thickness is not competitive with other thermal-control techniques, then the PCM technique can be eliminated from further consideration.

Contact Resistance and Three-Dimensional Effects

Errors introduced by contact resistance and three-dimensional conduction effects were neglected in the preceding analysis. These errors can be significant, as the following discussion indicates.

Consider a filler material of aluminum honeycomb in a container 1 cm thick. The thermal conductivity of the PCM is so much less than that of aluminum that the total equivalent conductance through the PCM/honeycomb composite is approximately $k_{Al}A_{Al}/L$. If a relatively high-conductivity metal-filled adhesive is used to bond the honeycomb to the cold plate, the thickness of adhesive between the honeycomb and cold plate will represent a thermal resistance between the honeycomb and cold plate. The resistance of the adhesive will be $L_{adh}/k_{adh}A_{adh} \sim L_{adh}/k_{adh}A_{Al}$. The total resistance through the package now becomes the sum of the two series resistances, namely

$$R_{eq} = \left(\frac{L_{adh}}{k_{adh}} + \frac{L}{k_{Al}} \right) \frac{1}{A_{Al}} \quad (11.22)$$

Since k_{adh} will at best be only a few percent of k_{Al} , perhaps 3%, an adhesive thickness of 3% L or 0.03 (1 cm) = 0.3 mm will cause the resistance R_{eq} to be double the value obtained by neglecting the adhesive resistance. Since the heat entering the package must pass through both resistances, $Q = \Delta T/R_{eq}$, doubling the R_{eq} will double the ΔT through the package, and consequently the temperature excursion of the component will be doubled. In addition, bubbles can form in the adhesive upon curing, reducing the effective cross-sectional area of the heat path through the adhesive and thereby increasing the resistance further. These resistances

can obviously cause the component temperature to rise appreciably above the value predicted by the idealized one-dimensional analysis presented earlier. These effects indicate the need for a metal-to-metal contact that could be accomplished by some form of welding, soldering, or integral fabrication of filler and cold plate.

The simplified one-dimensional analysis presented earlier is the first step in determining if a PCM approach offers potential advantages for a particular design problem. However, because the one-dimensional analysis does not account for three-dimensional heat-spreading effects in the plate and PCM, one must still perform a detailed computer analysis. Such an analysis is likely to show that the PCM, while still advantageous, is not quite as good as the simplified analysis had suggested.

Containment Considerations

The design of the container for a PCM package must take into account both structural and thermal considerations. Structural considerations include the need for the package to be leakproof (for a liquid PCM) and to withstand all imposed static and dynamic loads. A primary thermal consideration is the requirement for the container to be integrated into the thermal-protection package without degrading system performance.

A major problem in the design of PCM containers is the need to accommodate the volume change that occurs when the contents melt or freeze. Several methods have been developed to deal with the phase-transition volume change; one is shown in Fig. 11.16. An elastic bellows between the cold plate and the opposite wall is prestressed in tension during the fill process. After filling is complete, the bellows exerts a compressive load on the liquid PCM. When solidification occurs, the bellows further contracts and still maintains a compressive load on the PCM. A bellows container using stainless steel as the bellows material was built and tested.^{11,10} No filler material was used in the bellows container, but a filler could be attached to the cold plate in such a container. The major advantage of a bellows container is that no void or gas volume must be left in it to provide room for PCM expansion upon melting. Since void or gas volume could cause a decrease in heat transfer within the container, use of the bellows container does have a distinct

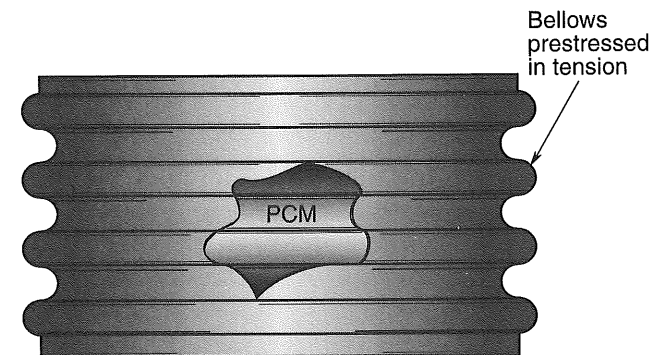


Fig. 11.16. Elastic bellows container.

thermal advantage over other techniques. However, the nonrigidity of the container and the cyclical change in loading could cause structural or leakage problems. The design engineer should consider these risks. The more commonly used container is the rigid container that has void or gas volume for expansion of the PCM during melting. Rigid containers have been used on the Lunar Roving Vehicle and on the Skylab Cluster. Such a container is shown in Fig. 11.17. In this figure, the void region is shown at the top, where it would be under terrestrial gravitation, but in a "0-g" environment the void volume would occupy different regions of the container.

A significant problem in designing the rigid container is the sizing of the void volume. If the container were totally vacuum-tight and evacuated prior to flight, theoretically the void volume required would merely be the volume change upon expansion of the PCM, namely,

$$\text{Void volume} = V_L - V_S = m_{\text{PCM}} \left(\frac{1}{\rho_L} - \frac{1}{\rho_S} \right) \quad (11.23)$$

However, gas will be in the void volume while the solid phase exists in the container, as a result of equilibrium vapor-pressure formation above the solid phase and prelaunch molecular diffusion through the minute holes that will exist in joints and seams of the container. Regardless of the pressure of this gas above the solid phase, when complete liquefaction occurs, a large pressure will be set up within the container since no volume exists for the gas phase to occupy. Therefore, sufficient volume must be added to the container to maintain trapped gases at a reasonable pressure.

Some designers of rigid containers^{11.11} take the most conservative view that the pressure above the solid phase has reached atmospheric pressure because of leaks before launch. With the aid of Fig. 11.18, one sees from the ideal gas law at constant temperature that the relation between maximum pressure and total volume is

$$P_{\text{max}} = P_{\text{atm}} \left(\frac{V_T - V_S}{V_T - V_L} \right) = \left[\frac{V_T - \frac{m_{\text{PCM}}}{\rho_S}}{V_T - \frac{m_{\text{PCM}}}{\rho_S}} \right] (P_{\text{atm}}) \quad (11.24)$$

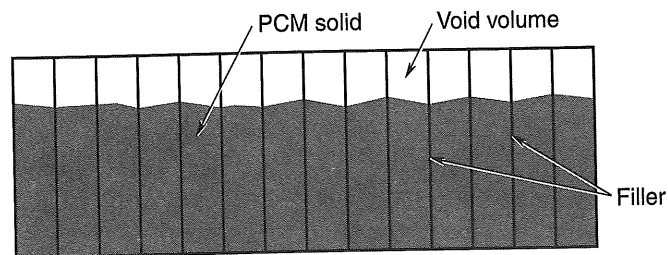


Fig. 11.17. Rigid PCM container.

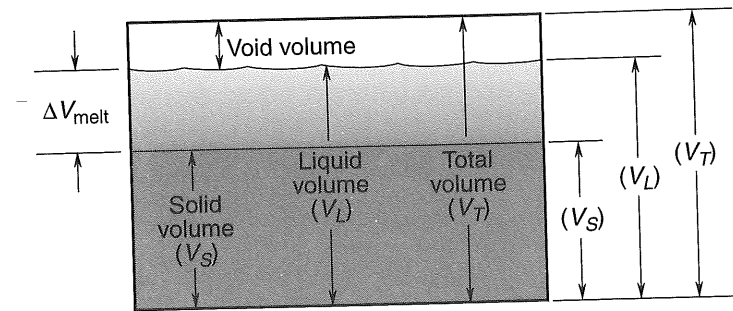


Fig. 11.18. Volume relationships for rigid containers.

The container should therefore be designed to withstand the P_{max} structural maximum loading associated with the final choice of V_T . If the PCM liquid will rise appreciably above the melt point at any time during planned operation, the thermal expansion of the liquid should also be considered in determining the total container volume.

The effects of the void or gas volumes within the container on heat transfer are hard to estimate quantitatively. However, such void spaces will decrease the conduction heat transfer below that for the idealized void-free models currently assumed for analysis, especially if voids were to form between the cold plate and PCM or between the filler and PCM. In general, degradation as a result of voids should be least for materials with high wetting tendencies, i.e., those that cling to the solid metallic surfaces within the package. The previous discussion demonstrated that materials with very small percentage volume changes during phase transition cause fewest thermal and structural problems for the design engineer.

The bonding between any filler material present and the cold-plate portion of the container is a problem area previously discussed. To prevent thermal resistance at the bond, use metal-to-metal bonding. Soldering and brazing techniques can be used for a particular application if welding is not possible.

A slightly different packaging technique can improve thermal performance of PCM systems that are to be used for one-duty-cycle components. Such components generate high amounts of heat for a period of time and then cease operation, never again to be activated. Such a component can be placed in thermal contact with a PCM package to keep it relatively isothermal for its short life. The PCM package essentially absorbs, via phase change, all the energy generated by the component, and refreezing after the cycle is unnecessary. The container technique shown in Fig. 11.19 could be used for such an application.

The spring initially could be compressed so that throughout the melt process it would hold the solid firmly in contact with the cold plate. The liquid would pass to the bottom and the cold plate would remain virtually isothermal at the melting-point temperature without the addition of filler materials to the package. In a similar technique presented by Fabian and Vaccari,^{11.10} a pressurized bladder performs the same function as the spring.

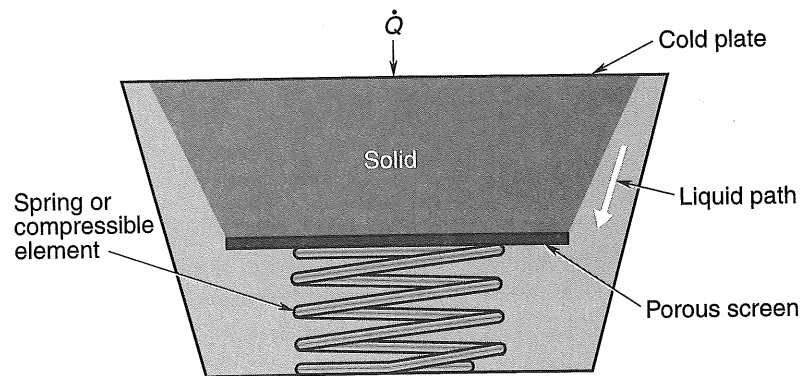


Fig. 11.19. One-duty-cycle PCM container.

Material Properties and Compatibility

In selecting container and filler materials, the engineer must consider their thermal and mechanical properties as well as the compatibility of PCM materials with their containers. Metals have been the universal choice for PCM containers and for fillers because of their high thermal conductivity, yet none of the PCM candidate materials have been rigorously tested for long-term compatibility with these aerospace metals. Generally the concern is corrosion of the container metal by the PCM itself or by some impurity in the PCM. Of course, some impurities have no effect on the compatibility of the basic materials, and a few types of impurities even inhibit corrosion.

Material Corrosion

The primary mode of material corrosion of concern in PCM technology is chemical corrosion. Generally, PCMs of the salt-hydrate-metallics and fused-salt categories are the most corrosive. Corrosion by PCM impurities can occur when the contaminant is a metal ion such as Pb^{+2} and the base PCM material, such as water, acts as an electrolyte between the ion and the container metal.^{11.12} The result is that ionization removes the aluminum from the container. This form of corrosion can occur for a large variety of combinations of container metals and contaminants. None of the combinations are documented with regard to severity of corrosion in a PCM application. Furthermore, the concentration of the contaminants along with several other variables influences the extent of corrosion. For these reasons, specific combinations to avoid are not presented. Bregmon^{11.13} and Bosick^{11.14} present the limited information that is available. A general guideline, however, can be found in Table 11.5, where any metal listed will react with any ion listed below it. For example, iron (Fe) will dissolve in a nickel (Ni) solution, plating out nickel metal. There are exceptions to the general trend indicated in the table, so design decisions regarding contaminants should not be based solely on this data.

Table 11.5. Potentials of Electrochemical Reactions

Element	Reaction
Beryllium	$Be^{2+} + 2e^- = Be$
Aluminum	$Al^{3+} + 3e^- = Al$
Titanium	$Ti^{2+} + 2e^- = Ti$
Manganese	$Mn^{2+} + 2e^- = Mn$
Vanadium	$V^{2+} + 2e^- = V$
Zinc	$Zn^{2+} + 2e^- = Zn$
Chromium	$Cr^{3+} + 3e^- = Cr$
Gallium	$Ga^{3+} + 3e^- = Ga$
Iron	$Fe^{2+} + 2e^- = Fe$
Chromium	$Cr^{3+} + e^- = Cr^{2+}$
Titanium	$Ti^{3+} + e^- = Ti^{2+}$
Thallium	$Tl^+ + e^- = Tl$
Vanadium	$V^{3+} + e^- = V^{2+}$
Nickel	$Ni^{2+} + 2e^- = Ni$
Tin	$Sn^{2+} + 2e^- = Sn$
Lead	$Pb^{2+} + 2e^- = Pb$
Hydrogen	$2H^+ + 2e^- = H_2$
Tin	$Sn^{4+} + 2e^- = Sn^{2+}$
Copper	$Cu^{2+} + e^- = Cu^+$
Copper	$Cu^{2+} + 2e^- = Cu$

Corrosion Inhibitors

A corrosion inhibitor is a substance used to reduce the corrosion rate of metals by materials. The first step for selecting a corrosion inhibitor for a specific system is a thorough study of the system itself. Inhibitors that are valuable for some applications can be harmful in others. Extrapolation from one system to another has caused considerable damage to many industrial systems. Although inhibitors for some corrosion problems can be similar to inhibitors for others, this similarity should be regarded as coincidence. The lengthy procedures required for the development of a good corrosion inhibitor explain why most inhibitors are developed by specialists.^{11.13}

There are two basic categories of inhibitors.

- **Oxide films**, such as those formed on aluminum, titanium, and stainless steel, form a protective layer that is inert to many PCMs. When corrosion resistance needs to be increased, the oxide coating is treated to make it thicker.

- **Additives** form protective coatings on the metal surface to provide physical protection against corrosive attack. These include long-chain aliphatic acids and aqueous solutions of sodium bicarbonate and sodium phosphate. These inhibitors can be added in small amounts to the PCM to decrease corrosion. (A common use of this type of additive is rust inhibition for radiators, steam boilers, etc.) Although added to the bulk of the PCM, they adsorb onto the metal surface to form a continuous layer.

There are many possibilities for effective applications of inhibitors. Suggested inhibitors for specific PCM/metal combinations are listed in following paragraphs, and Bregmon^{11.13} provides additional information.

PCM Container and Filler Materials

Three metals are currently used for PCM containers: aluminum, titanium, and stainless steel. They have high strength-to-mass ratios and are corrosion-resistant. All have been widely used in aerospace technology.^{11.15} Although stainless steel is heaviest, it is more elastic and can thus accommodate PCM volume changes. Each of these metals has its own advantages and special characteristics. A designer must choose the metal or metal combination most suitable for a particular application. Other metals or metal alloys may also be highly desirable and merit consideration.

Aluminum

Because of aluminum's low density, high thermal conductivity, and corrosion resistance, many PCM designers use it for containers and fillers. Aluminum is amphoteric: it can form compounds with PCMs that are either strong acids or strong bases (alkali hydroxides). It forms salts with strong acids (chlorides, nitrates, and sulfates) and aluminates (AlO_2^-) with bases.^{11.16} PCM materials that are compatible with aluminum are shown in Table 11.6.^{11.12,11.7} Inhibitors that may be useful for reducing corrosion of aluminum with various PCMs are shown in Table 11.7, and further information can be obtained from Van Horn^{11.17} and Dambal and Rama Char.^{11.18}

Table 11.6. PCMs Compatible with Aluminum

Category	PCMs
Acids	Acetic, elaidic, myristic, stearic, benzoic
Alcohols	Ethylene glycol
Dry inorganic salts (except salt hydrates)	Most fused salt eutectics
Miscellaneous organics	Acetamide, methyl fumarate, paraffins, polyethylene glycol, tristearin, oxazoline waxes, silicates
Oxidizing PCMs	(Only if protective aluminum oxide film is present)
Sulfur compounds	Most PCMs that are inorganic sulfides or organic sulfides
Water	High-purity: distilled or deionized water

Table 11.7. Corrosion Inhibitors for PCMs in Aluminum Containers

PCM Category	Corrosion Inhibitor
Acids	Soluble oils, alkyl arylsulfates, and amines
Alkaline compounds	Silicates with a high ratio of silicate to soda
Water	Borates, silicates, nitrates, phosphates, soluble oils

Aluminum can be soldered, brazed, and welded. Soldering aluminum differs from soldering other common metals in several ways. The refractory oxide coating on aluminum requires special fluxes. With aluminum, resistance to corrosion depends much more on solder composition than it does for most other metals. Aluminum-to-aluminum joints are generally superior in strength to joints between aluminum and dissimilar metals.^{11.19} Silver solders commonly used for joining other metals cannot be used for joining aluminum because none of them has a low enough melting range. The various types of solders and fluxes are described in Reference 11.19.

Titanium

Titanium is superior to all other metals on a strength-to-mass basis^{11.20,11.21} and has outstanding corrosion resistance. It is one of the few metals that would be suitable for use with gallium and alloys of gallium, since these PCMs are very destructive to most metals, especially aluminum. This resistance is a result of the formation of a protective film, promoted by oxygen or oxidizing agents.^{11.22} Titanium's thermal conductivity, however, is about 1/16 that of aluminum. Table 11.8 lists PCMs that are compatible with titanium under ordinary service conditions.

Stainless Steel

In PCM technology, stainless steels have been used for containers or parts of containers. Stainless-steel bellows were used in containers because of their elasticity in adjusting to continual volume changes caused by PCM melting and freezing. The advantages of great strength, elasticity, and corrosion resistance have qualified this metal for some PCM applications.^{11.12,11.23,11.24}

Table 11.8. PCMs Compatible with Titanium

Category	PCMs
Acids	Acetic, chloroacetic, stearic, lactic, salicylic, succinic
Salts	Most inorganic and organic salts, magnesium sulfate, sodium chloride, sodium sulfate, potassium chloride
Miscellaneous	Water, gallium, hydrogen sulfide

Stainless steels can be soft-soldered and silver-soldered. No problems such as sensitization, hardening, or tempering arise at the low temperatures involved in soldering. All stainless steels can be brazed, and no fluxes are required. Welding with few problems is common. Corrosion resistance is a major consideration in the selection of a stainless-steel alloy. Basically, corrosion resistance of all stainless steel depends upon its chromium content. Chromium as a pure metal is very active, but it occurs as an oxide in stainless steel, usually $\text{FeO}\cdot\text{Cr}_2\text{O}_3$. Stainless steel is inert to many environments as a result of the formation of this oxide.^{11.24} Since the alloys vary so widely in corrosion resistance, researching specific alloys is advisable. Generalizations about their corrosion resistance are difficult to make, but all stainless steels are moderate to excellent in this area.

The PCM Design Process

To proceed quickly and efficiently in the design of a PCM thermal-protection system, the designer should follow a process similar to the following.

1. Choose the PCM with the best properties, as described previously, whose temperature range matches the temperature range of the component.
2. Perform thermodynamic analysis to: define thermal flux and storage requirements; determine most efficient heat dump for cyclical components; size radiators, thermal straps, heat pipes, or other heat dump methods; and determine initial estimate of PCM quantity required.
3. Perform combined thermodynamic and heat-transfer analysis to obtain mass, thickness, and temperature excursion as functions of filler amount. Pick the minimum mass and thickness that will meet temperature-excursion requirements.
4. Select a compatible container material and design container according to guidelines given earlier.
5. Conduct necessary detailed thermal analysis to verify the performance of the PCM system.
6. Conduct necessary experimentation to prove the performance and reliability of the PCM system.

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