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Review of Classification of PCMs, with a Focus on the Search for New, Suitable PCM Candidates

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Abstract: With a growing number of PCMs and new, suitable PCM candidates, an overview is not only important, but also increasingly complex. Classification of PCM was thus changed significantly in the past decades. A review of classification of PCMs from recent years shows that not only different classification criteria are used, but more important that they are often mixed, used inconsistently, even without a clear goal. Focusing on the main goal of current classification schemes, to give an overview of the material options for the search for new, suitable PCM candidates, including already established PCMs, a consistent classification is developed in a desktop study. For this, first, the general options for classification criteria are reviewed, and then the appropriate ones selected. Then, based on them a new, revised PCM classification is suggested. It is specifically detailed with regard to mixtures; for binary mixtures it is based on a literature review performed within the study. The result also stresses the importance of specific R&D: for pure substances the sources and the chemical modification, and for mixtures their optimization by new compositions, additives, etc.

Keywords: PCM; classification; criteria; pure substances; mixtures; alkane; salt; salt hydrate; metal

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1. Introduction

1.1. Background on PCMs

Thermal energy storage (TES), often also called heat and cold storage depending on the application, plays a crucial role in the energy system today, and will even more in the future. Different effects can be used for TES; one is a phase change, between solid and liquid or sometimes different solid phases. These phase changes typically occur in a narrow temperature range. If phase change is at a single temperature the heat is also called latent heat as it cannot be sensed without a temperature change. Materials that store a significant amount of heat this way are called Phase Change Materials (PCMs), often also latent heat storage materials (even if some temperature change is involved).

The ability to store a significant amount of heat in a narrow temperature range results in two usage fields (Mehling et al. [1]): thermal energy storage (heat or cold storage) with high storage density (per mass or volume) in a small temperature range, and passive temperature stabilization (temperature control). Corresponding to these, PCMs are used today commercially in a wide range of applications: in buildings (for space cooling, space heating, and preparing domestic hot water), in logistics (mainly the cold chain), for the human body (for heating or cooling) including medical applications, in mobility, in electronics, as well as industrial processes (Mehling et al. [2]). And there are many other potential applications, with intense R&D going on at all levels from the PCM to whole systems and also system integration; e.g. in the food area (Mehling [3]) for solar cooking and water desalination, or in the energy system for solar thermal power plants and electro-thermal energy storage (also called Carnot batteries).

The most common PCM is water, with a phase change temperature T_{pc} between solid and liquid at 0 °C, and an enthalpy change on phase change $\Delta_{pc}h$ of 333 kJ/kg or 306 kJ/L (at lowest density of 0.92 kg/L). For other application temperatures other materials with suitable T_{pc} have to be used. Well known are paraffins, fatty acids, alcohols, and salts, as well as mixtures of two or more materials, e.g. eutectic mixtures of water with salts, salt hydrates, or mixtures of salts. And many more are investigated and developed today to keep up with the growing demand for PCMs and the increasing range of applications. An overview on existing PCMs and new, suitable candidates, including classification, is thus important. At the same time the growing number of materials and material classes makes it increasingly complex.

1.2. Review of Classification of PCMs as Used in the Early Years

Materials are commonly classified, meaning organized in classes (also called groups, categories, types), with respect to a criterion. As a result, materials being similar are in the same class, while those being dissimilar are in different classes. Classification is a common approach, practically used everywhere, because it allows simplification, by avoiding details. Depending on the goal and focus of classification, materials can be classified with respect to different criteria, and as a result are then grouped differently. It can also happen that members of a class are similar with regard to several criteria if they are connected; e.g. metals have a metallic bond, so due to the free electrons are good thermal and electrical conductors. Material classes used in physics and chemistry refer mainly to the bond type (e.g. metallic, covalent, ionic, van der Waals, or hydrogen bonds, being polar or non-polar), arrangement of atoms in molecules (differing by functional groups like alkanes, fatty acids, alcohols, being linear or branched, and being short or even polymers) and arrangement of atoms and molecules in bulk (e.g. crystalline or amorphous).

For PCMs, the most basic function is thermal energy storage (heat and cold storage) described by the enthalpy h(T), often simply enthalpy change on phase change $\Delta_{pc}h$ and phase change temperature T_{pc} (Mehling [4]). As they are the primary selection criteria of PCM for an application, it is straight forward to combine material classes with them. As a result, classification started with the few, early PCM material classes, and their typical enthalpy change on phase change $\Delta_{pc}h$ and phase change temperature T_{pc}, as in Figure 1. Early PCM material classes were the salts (nitrates, hydroxides, chlorides, carbonates, fluorides), salt hydrates, chlathrates, water, and specific eutectic water-salt mixtures, all being inorganic materials, then paraffins, fatty acids, and sugar alcohols, all being organic, and the polymers polyethylene and polyethylene glycols. They can also be classified as low, medium, and high temperature PCM.

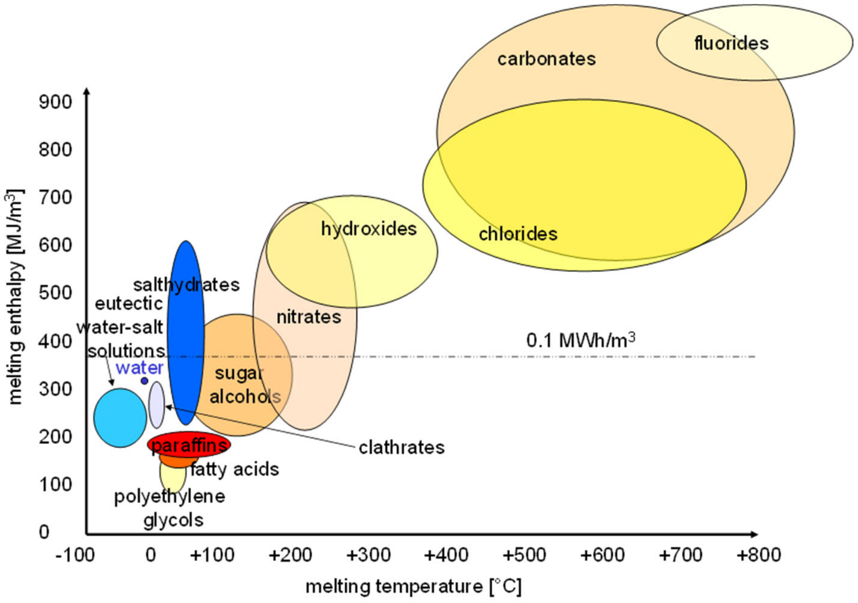

Figure 1. Classes of materials that can be used as PCM and their typical range of melting temperature and melting enthalpy (Mehling et al. [1], source: ZAE Bayern).

In the early years of PCM development, the 1970s, the number of material classes investigated for PCMs was small. This remained unchanged until the late 1990s, as the focus was on improving known PCMs. The following decade R&D on PCMs intensified, including that more material classes were investigated. In the 2020s then the number of potentially useful PCMs literally exploded. This was not only due to more focus on material classes like alcohols, esters, or polymers. It was mainly due to the combination, leading to an increasing number of mixtures. This started with mixtures within a material class, e.g. salt-salt or alkane-alkane mixtures, and soon also mixtures between material classes. Thus, overviews with material classes in a $\Delta_{pc}h$ versus T_{pc} graph, like Figure 1, cannot give a complete overview anymore.

1.3. Review of Classification of PCM as Commonly Used Nowadays

R&D for specific applications nowadays has access to lists of $\Delta_{pc}h$ versus T_{pc} of many commercial PCM. Such lists are preferred to identify a suitable PCM, instead of a simple overview of material classes. They give not only a more complete, detailed overview (e.g. specific product), but moreover from product data sheets information is available on density, volume change on phase change, thermal conductivity, long term (e.g. cycling) stability, material compatibility, etc., maybe even a cost value.

Additionally, simple overviews like Figure 1 are nowadays not possible anymore; this is not only due to the growing number of materials investigated, and even more the number of combinations by mixing. On top, mixtures can have very different properties compared to their components, e.g. mixtures of salts typically have lower T_{pc} than their components. Even salts melting at room temperature are known today. Consequently, it can be expected that classification nowadays focusses more on materials and mixtures, and less on the properties of them. Inherently the use of classification thereby changes; it is not useful to select PCMs for an application, but rather has information useful for the development of new PCMs. Classification of PCMs is used to give an overview, e.g. for the search for new, suitable PCM candidates.

To get an overview on the current use of PCM classification, an internet search was performed using as key words “PCM classification” and “LHS material classification”. The general result, meaning common features, is reviewed in the following (an individual discussion is omitted to avoid excessive, needless references).

Thermal energy storage, TES, can be subdivided in different ways, and is often done in classification. For the materials the terms phase change material, PCM, and latent heat storge material, LHS material, are often used synonymously, despite that they express different things (many PCMs do not change phase at constant temperature). The result of the search shows that for materials most common is using PCM, while the method, if mentioned, is termed latent heat storage [5,6]; this shows Figure 2. The term used for the start of material classification is thus PCM.

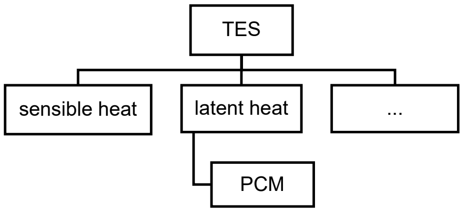

Figure 2. Classification of TES, with methods below, and then materials used.

Based on classification in the early years of PCM R&D, with few material classes, it is nowadays still common (e.g. Kavya and Ramana [7], or Podara et al. [5]) to classify first by organic, inorganic, and additionally eutectic, and then use more specific material classes; this shows Figure 3 schematically.

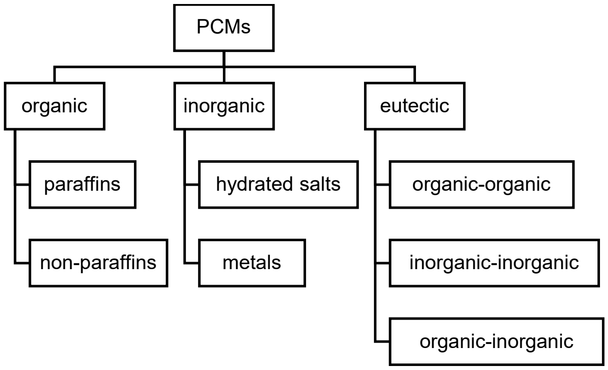

Figure 3. Classification of PCMs, with material classes in different detail.

However, the first classification level is erroneous. Organic and inorganic are complementary, except mixtures of both; in addition, eutectic does not mean mixture in general but denotes very special mixtures.

Another common way to classify PCMs is using the type of phase change: solid-solid and solid-liquid. Podara et al. [5] e.g. use this as first classification level, and then subclassified as previously discussed, with non-paraffin and polymers getting own material subclasses. This shows Figure 4 schematically.

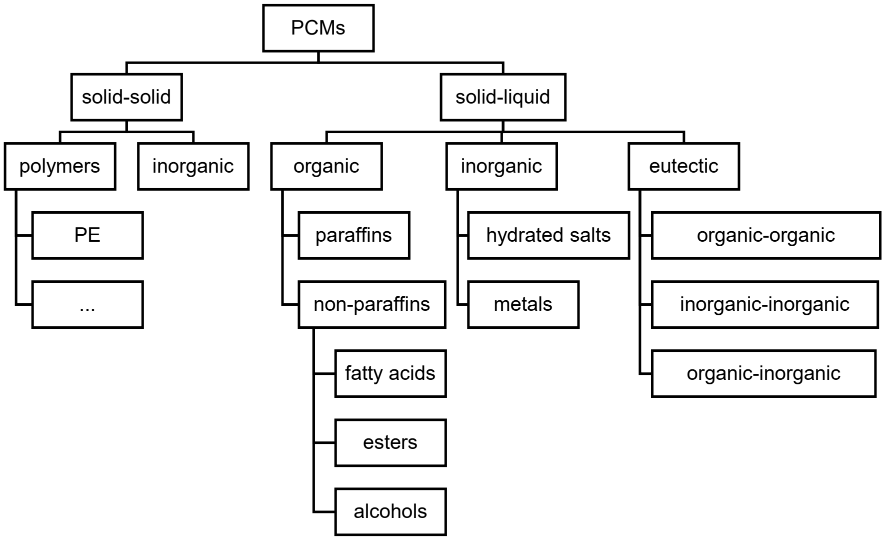

Figure 4. Classification of PCMs, with type of phase change, then material classes in different detail.

This has several inaccuracies. Many paraffins, actually alkanes, have besides a solid-liquid also a solid-solid phase change. And many polymers, called thermoplastics, become plastic instead of liquid, meaning flow only under an extra force, while liquids flow under their own weight. PE is one of them. By crosslinking the plastic behavior can be eliminated, thus that the phase change becomes solid-solid. Jouhara et al. [8] are more specific, e.g. also mention grafting as option. The term "shape-stable" is also often used in this context, however it has no generally accepted meaning, and is thus not discussed here further.

The crucial focus on PCM being mixtures or not, already discussed above (Figure 3), was also used by Gunasekara et al. [9] but expressed directly: instead of organic, inorganic, and eutectic, the latter being falsely used for mixtures, they use pure components and blends (several pure components; binary, ternary …). Their approach is schematically shown in Figure 5.

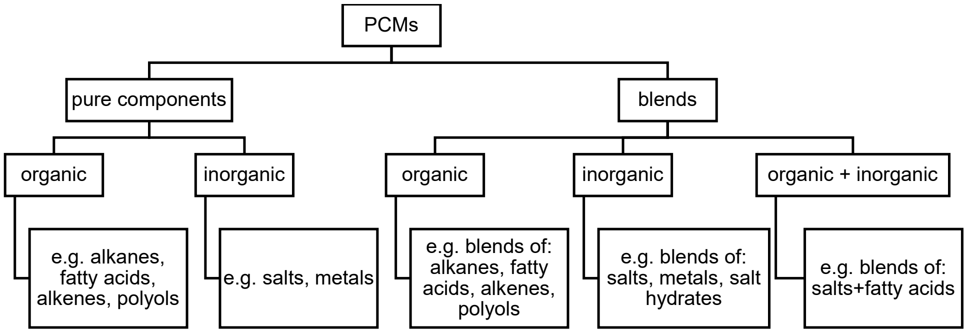

Figure 5. Classification of PCMs, with focus on being mixtures or not, then material classes in different detail.

However, the terms used are not precise. The term used in chemistry (e.g. by Atkins [10] or by Brown et al. [11]) is mixture, and not blend, and components are what makes up a mixture, so no pure component exists. Phase diagrams of mixtures depict components as extremes. Single component and mixture of several would be better, but component is misleading. E.g. SiC is composed of Si and C; the components in the binary phase diagram of SiC are Si and C. Still, SiC is not a mixture; it exist only in the 1:1 composition. Correct terms are pure and non-pure substance, as will be explained later in detail (section 3.1).

2. Analysis of weaknesses

Generally, of course, but specifically because materials research involves specialists from various fields, the use of correct and if possible well-established terms is mandatory. Already here weaknesses exist.

Next, including materials which are investigated for use as PCM but not commonly applied as PCM yet, e.g. esters (Figure 4) and alkenes (Figure 5), it is clear that the focus of common PCM classification nowadays is development-oriented, giving an overview of the wide range of options for PCM selection. In literature the goal is however usually not mentioned, so any reasoning behind a chosen classification is unclear. At best the motivation to give an overview is mentioned. For the further investigation here, the goal of classification should thus be to give a simple overview, avoiding unnecessary details, of the material options for the search for new, suitable PCM candidates, including already established PCMs.

Classification, other than just listing materials, separates material classes from each other, depending on classification criteria. This could be the type of phase change (solid-solid, solid-liquid …), the chemical nature and composition, but as well the temperature range where phase change occurs, and many others. In literature classification criteria are never mentioned, just classes given (e.g. organic and inorganic). Often it is possible to guess, however leaving the criterion unclear has several negative consequences. First, not giving the criteria the overall idea of the systematics used for classification remains unclear, specifically why a criterion is used, and why in a specific order regarding the goal of classification. Second, not specifying the criteria can easily lead to inconsistent classes within a criterion. And finally, not giving the criteria can even lead to the use of wrong terms without noticing. For example, for the type of phase change sometimes solid-solid, solid-liquid, and liquid-gas are noted, but liquid-gas is not included when talking about PCMs. Also, solid-solid transitions exist in alkanes and sugar alcohols by their very nature, while grafted polymers and polymers like PE which are by their nature undergoing a solid-liquid phase change can be made to undergo a solid-solid phase change by chemical crosslinking. It is thus necessary to specify for PE if it is crosslinked, and e.g. for alkanes that the phase change with the main thermal effect is meant. Regarding the chemical nature, use of organic, inorganic, and eutectic, is already wrong as organic and inorganic are complementary thus that there is no room for a third class. If they are meant to refer to pure substances as the overreaching class, then it has to be stated clearly. And the complementary class is then non-pure substances, meaning mixtures. Eutectics are mixtures, however only a very special type of them, one with a eutectic phase transition. Being organic or inorganic has also no specific meaning with regard to the goal of classification, thus why use it at all? Covering a large range of materials, not just few like paraffins, salt hydrates, and salts, it does not even indirectly give a specific information. Still general properties are attributed in literature. For example, Jouhara et al. [8] stated that organic PCM show no supercooling, but that inorganics do. Correct is however that while many organics show little supercooling in bulk, e.g. alkanes have been shown to supercool in microscopic volumes, and many sugar alcohols are known to supercool dramatically. Comparing only paraffins and salt hydrates, the mass specific $\Delta_{pc}h$ is often in a similar range, however due to the typical density the volume specific $\Delta_{pc}h$ of salt hydrates is typically larger. But if also including sugar alcohols a general statement that organics have lower volume specific $\Delta_{pc}h$ is becoming wrong. And in mixtures $\Delta_{pc}h$ tends to decrease, thus that mixing two components with large $\Delta_{pc}h$ can lead to a mixture with small $\Delta_{pc}h$ for any kind of materials.

In summary, what can be found in literature is often rather a collection of things than a real classification. The goal of classification is unclear, often the criteria used for classification, generally their justification, as well as their order. Even use of wrong terms is common. Good classification is however essential, specifically with the increasing number of material classes and materials mixed.

After the review of classification of PCMs as commonly used nowadays, identification of weaknesses, and identification of the common goal of classification, namely to give an overview of material options for the search for new, suitable PCM candidates, including already established PCMs, next is to develop better classification. This is done in section 3. As first step, classification criteria are reviewed. Next, based on them and the goal of classification the most useful classification criteria are then selected. Using them a new classification is suggested, which is consistent, and useful.

Before starting, crucial is that the scope of the review here is the materials used for TES, thus PCMs. Not covered are PCM composites, and also not encapsulated PCMs; they are separate topics.

3. Development of Consistent, Useful Classification

3.1. Review of Options for Classification Criteria

Classification schemes should have a well-defined goal and have a corresponding systematic approach, thus use the same criterion on a level, possibly different ones on different levels, and use correct terms. The introduction comprises an overview on typical classification schemes found in current literature, and the classification criteria used in these examples could be used to develop new, consistent schemes. However, in the long term, to find the most useful schemes an overview on possible criteria is needed; then the best, most useful, can be selected. For a good overview a systematic search for criteria is needed. This search was done, and the identified criteria are discussed individually now in the following section. Table 1 gives an overview.

Table 1. Overview on options for classification criteria (and possible classes).

Thermal properties (for heat storage and heat transfer …)	
	phase change enthalpy, more precise enthalpy change on phase change $\Delta_{pc}h$
	phase change temperature T_{pc} (e.g. low, medium, and high temperature PCM)
	thermal conductivity
Chemical properties (with regard to safety, compatibility, sensitivity to change of composition)	
	safety, specifically combustibility, fire hazard …
	compatibility, specifically corrosivity …
	sensitivity to loosing matter to the ambient or taking up matter from it
Phase change properties	
	type of phase change (solid-solid, solid-liquid …; the one that is used, thus not a material property)
	type of phase transition (peritectic, eutectic, …)
	formation of phases with different composition (congruent, incongruent, or semicongruent melting)
Composition (chemical / physical)	
	organic, inorganic, or a combination
	pure substance (element, chem. compound) or non-pure substance (homogeneous, heterogeneous mixture)

	material class (for elements e.g. metal, for chem. compounds e.g. alkane, alcohol, fatty acid, salt, and for mixtures e.g. salt hydrate, gas hydrate, etc. thus giving information on the components as well as how the components interact)
	molecule structure (specifically referring to chem. compounds alone as well as in mixtures: linear, branched, grafted, crosslinked … mono-, oligo-, polymer)
Production and life cycle	
	source (bio-based, fossil-based, food-based, waste-based, extracted or modified by a chem. process)
	availability (commercial product, lab scale produced, R&D …)
	sink (bio-degradable, landfill deposition, waste incineration, …)

To focus on crucial physical and chemical properties to apply a PCM is a first straight-forward approach. In a review "Analysis of Existing Approaches to Investigate Property Degradation of Phase Change Materials and Development of a New Systematic Approach" (Mehling [4]) basic functions of PCMs in applications for heat storage, and their corresponding physical or chemical properties for description were identified. The most basic function is "heat storage", described by the specific enthalpy h(T), or simplified by the phase change temperature T_{pc} and associated enthalpy change on phase change $\Delta_{pc}h$. Early classifications that focused on the application and the selection of useful material classes used T_{pc}, to classify as low, medium, and high temperature PCM. Another basic function needed for heat storage is heat transfer, described by the thermal conductivity. Together they are thermal properties (Table 1). To focus on protecting the PCM from the ambient and also the ambient from the PCM (Mehling [4]) is another option. Terms used for classification are safety (combustibility, fire hazard …), compatibility (corrosion …), and not to forget sensitivity to losing matter to the ambient or taking up matter from it. They are chemical properties, often classified by being suitable or not, referring to a given requirement. To focus on the phase change and some of its related properties is also directly related to heat storage, as the basis of using PCM is the phase change. The most obvious criterion is the type of phase change, for PCMs being solid-solid or solid-liquid. The type of phase change is relevant in many ways, but not well defined and often misunderstood with regard to its consequences. First of all, it refers to the type of phase change that is used. E.g. all alkanes have a solid-liquid phase change which is used for TES, many also a solid-solid phase change that is not used or plays a minor role. For some sugar alcohols and grafted polymers it is the reverse: a solid-solid transition is used, and a solid-liquid transition at higher temperature is not used to keep advantages of remaining solid. To remain solid has several advantages, is however often misunderstood as that a PCM needs no encapsulation; but e.g. sugar alcohols can still be attacked by humidity if they are not encapsulated. Another misunderstanding is using solid-solid transition synonymously to being shape-stable. Shape-stable can refer to solid-solid phase change of a PCM alone, but also to a PCM with solid-liquid phase change in a porous structure with stable shape. Not to be mixed up with the type of phase change is the type of phase transition: peritectic, eutectic, … A eutectic phase transition is a transition between a liquid and a solid, at a single temperature, where the solid is actually composed microscopically of two or even more solid phases of different composition. A peritectic phase transition is between a liquid and a solid and a single low temperature solid phase. If phases with different composition exist at the same time, and have different density, then gravitation (or centrifugal forces) can separate them if at least one phase is liquid. Separation leads to decomposition, macroscopically, commonly called phase separation or phase segregation. It reduces the amount of material with the correct composition and thus reduces the heat storage capability. The terms congruent and incongruent phase transition are used for description; congruent melting means all liquid and solid phases have the same composition, incongruent if different. For congruent melting already different compositions do not exist, as e.g. in pure substances. In eutectics the different solid phases, having different composition and density, usually (not always, Quant et al. [12]) form at the same time and then macroscopic phase separation does not occur. Salt hydrates undergoing a peritectic transition to an aqueous salt solution and a solid lower hydrate are termed semicongruent (Lane [13]). Often, gelling can be used limit separation, or separation can be removed by mixing or by diffusion if given enough time in the completely liquid phase.

To focus on composition (chemical / physical) is another approach, besides properties to apply a PCM. Often used is classification as organic or inorganic materials. Organic and inorganic are complementary, and their combinations can be used for mixtures. However, with regard to classification important is that organic or inorganic have no clear relevance. With the wide range of materials investigated as PCM there are no common properties between all organics, e.g. alkanes, fatty acids, sugar alcohols, and the same for all inorganics, e.g. salts, metals, salt hydrates. Chemistry has better terms (e.g. Brown et al. [11]). Pure substances are elements, or chemical compounds. A chemical compound is composed of two or more elements in fixed (more specific integer) proportions, also called a stochiometric composition, e.g. in H_2O being H:O as 2:1. The origin are primary bonds, like molecules having covalent bonds or salts having ionic bonds, which are built by electron sharing or transfer. Pure substances have well defined physical and chemical properties due to their fixed composition, e.g. melting point and boiling point, while those of non-pure substances, which are any kind of mixture, vary with their variable composition. To split up into pure substance (with subclasses element and chem. compound) or non-pure substance (e.g. with subclasses homogeneous and heterogeneous mixture) is not only correct; it is moreover also more specific and useful compared to organic and inorganic e.g. due to the relation to many properties.

By far less well defined and structured are material classes. Some established are for elements e.g. metal, for chem. compounds e.g. alkane, alcohol, fatty acid, and for mixtures e.g. salt hydrate, gas hydrate, etc. thus for mixtures giving information on the components as well as how the components interact. Also, e.g. metal and salt also apply to their mixtures, e.g. a metal alloy is still a metal. Specifically referring to chem. compounds, the molecule structure is a criterion: linear, branched, grafted, or crosslinked, and referring to length and building blocks mono-, oligo-, polymer.

To focus on the production and life cycle is an approach that naturally comes with commercialization. Classification can be by the source, being e.g. bio-based, fossil-based, food-based, waste-based, including if the PCM is just extracted or if it is modified by a chem. process. However, care is needed. As mentioned before, many organics can e.g. be bio-based as well as from chemical processes incl. oil, and fossil based does not imply CO_2 emissions if a PCM is not burnt. Another criterion is the availability, being a commercial product, lab scale produced, or from R&D. And last, with increasing importance, a criterion is the sink, if bio-degradable, requiring landfill deposition, waste incineration, etc.

The search for criteria covered crucial physical, chemical, and phase change properties to apply a PCM, the composition of a PCM, and issues regarding production and life cycle. This systematic review of options for classification criteria assures that the main options of classification criteria have been found.

3.2. Selection of Classification Criteria with Regard to Goal and Focus

After gaining an overview on options of classification criteria, and the underlying systematics behind, the next step is to select useful classification criteria, including their rank, thus a classification scheme. Goal and focus of classification can vary and thus also the resulting classification scheme. In this review, the goal is now assumed to be the one that was identified as being widespread in the analyzed literature: to give an overview of the material options for the search for new, suitable PCM candidates, including already established PCM. Classification criteria must now be selected and ranked correspondingly.

The options of classification criteria (Table 1) cover physical, chemical, and phase change properties relevant to apply a PCM, the composition of a PCM, and also issues regarding production and life cycle. Obviously, for the search for new, suitable PCM candidates, the composition gives the primary criteria. The group comprising the thermal properties, chemical properties, and phase change properties, has no primary use for the goal set here. They are a result of material characterization after a PCM is developed, in some cases a general property of a material class, but in any case more relevant for materials selection. They are thus options for lower rank criteria. Some should also be avoided, or specified better for clarity. For example, the type of phase change is e.g. for materials that have solid-solid and solid-liquid phase change not clear in general and if it is

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specified as the phase change used then depends on a later choice. As another example, polymers can be subclassified as grafted, crosslinked, or nothing of both, or by the related phase change solid-solid or solid-liquid. The group comprising the criteria referring to production and life cycle has obviously also no primary use for the goal set here. The result of the evaluation of what is useful or not useful is thus, except phase change criteria, in accordance with the commonly used classification schemes discussed before, with a clear focus on composition. This result must be expected, as the goal defined here, development-oriented towards new PCMs, was derived from them.

The specific selection from the composition criteria, and the ranking for a classification scheme is next. The analysis showed that classification by organic or inorganic, which is wide spread, is rather useless. Being a pure substance (element or chem. compound) or non-pure substance (mixture) is the core to develop new PCMs; with a new material class investigated the number of combinations increases too. Subclasses homogeneous and heterogeneous mixtures (e.g. PCMs with phase separation) are not used. The material class is naturally following: for elements e.g. metal, for chem. compounds e.g. alkane, for mixtures e.g. salt hydrate. The molecule structure (linear, branched, grafted, crosslinked), specifically of chem. compounds alone as well as if being a component in mixtures, is a lower classification criterion; it can be added if it applies and if it is of interest. The latter also applies to secondary criteria, e.g. from phase change: the type of phase change (solid-solid, solid-liquid), type of phase transition (peritectic, eutectic, …), and formation of phases with different composition. They can be used to make specifications beyond that of the material. Actually, in some cases they are already inherent, e.g. for pure substances undergoing phase change solid-liquid the type of phase transition is automatically congruent melting. The following suggestion focusses, to be generally useful, on the primary criteria.

3.3. Suggestion of a New Classification of PCMs

As discussed, pure substance or non-pure substance is the top level of classification, with the subclasses element or chem. compound and respectively mixtures being binary, ternary, … as shown in Figure 6.

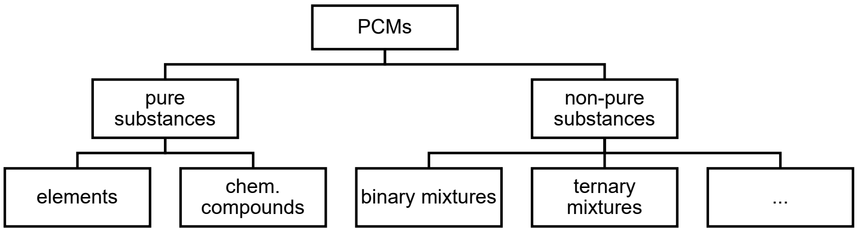

Figure 6. Top level of classification optimized for development of new PCMs.

These subclasses are discussed separately in the following, each with the most suitable criterion.

3.3.1. Pure Substances: Elements and Chem. Compounds

Elements are commonly split up into metals, non-metals, and semi-metals, based on their bond type which dominates their properties. Semi-metals are the transition between metallic and covalent bond. Figure 7 shows the elements split up that way, and examples that have at least been investigated as PCM.

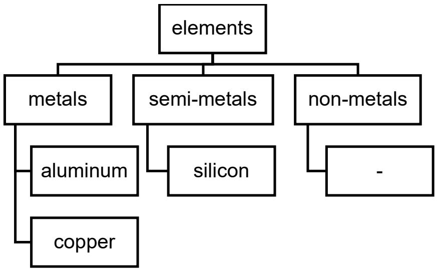

Figure 7. Classification of elements as PCMs.

Chem. compounds can be subdivided right away by material class, e.g. alkane, alcohol, which is straight forward, but not systematic and might lead to things being missed. In the previous discussion it was shown that chem. compounds must be formed by electron sharing or transfer, so must be molecules or salts. These could again be subdivided by their complexity, into small to large molecules and macromolecules (polymers), as well as simple and more complex salts like ionic liquids, as in Figure 8.

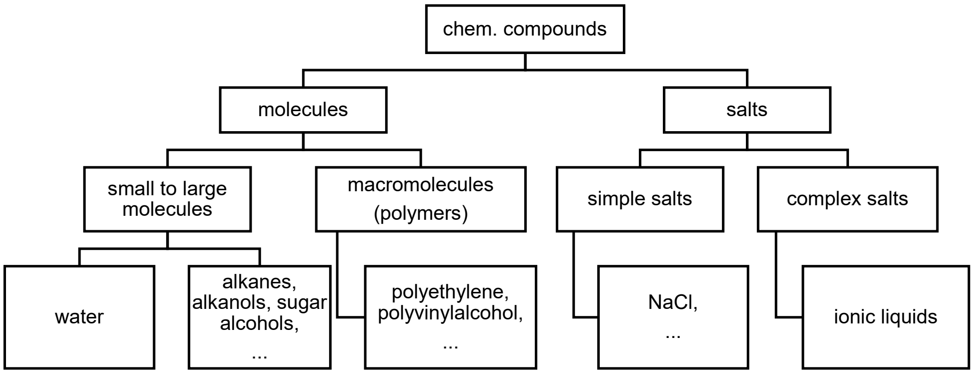

Figure 8. Classification of chem. compounds as PCMes, including several subclasses.

It is hard to give a systematic classification to all, e.g. polyethylene glycol is an ether and a polymer, and polyvinyl alcohol is a polymer as well as an alcohol, but it is nevertheless helpful to make an attempt. Alkanol (alkane derived alcohol) is thus used instead of alcohol, which would include sugar alcohols. Due to its importance, the size of the molecule is here deciding where e.g. an alcohol belongs to.

The small to large molecules subclass can then be filled with various material classes, in different ways. A systematic analysis of elements and simple chemical compounds was performed by Mehling [14], looking at data of 1120 different materials, and is giving some interesting insights for the next steps. Within small to larger molecules, materials suitable as PCM seem to be water and organic compounds, no other. Thus, it is logic to continue with both, separate due to their difference, as is shown in Figure 8. Water, the most widely used PCM, has actually been forgotten completely in the common classification schemes. Organic compounds (Brown et al. [11]) are compounds that contain carbon C, and hydrogen H, often in combination with oxygen O, nitrogen N, and other elements. Their importance here comes from the high variability and large number. The variability however also allows different ways of classification. Due to the four valence electrons of carbon C, the molecular structure of organic compounds can be

- saturated or unsaturated (due to double or triple bonds),
- branched or linear,
- cyclic or open chain.

Further on, organic compounds differ by functional groups (attached to the rest R), e.g.

- alcohols R-OH
- carboxylic acids R-COOH

- amines R-NH_2
- amides R-CON-R´R´´
- esters R-COO-R´

The base case, saturated, linear, and open chain, without a functional group, are the normal or n-alkanes. Unsaturated, branched, or cyclic molecules usually have lower phase change enthalpy compared to their counterparts, at given phase change temperature (see e.g. Mehling [14], Mehling and White [15]). However, there are exceptions, and even if a compound has lower phase change enthalpy it is possible that availability at low price might make it a good candidate; thus, these are not criteria of top choice. Consequently, using e.g. alkane instead of n-alkane in a classification allows to include the variation. Often the term paraffin is used synonymously, but paraffins are mixtures of various alkanes. Also, in most cases potential PCM compounds have just one functional group, and typically attached at the end of R. However, there are significant exceptions, e.g. alcohols useful as PCM can be classified further as diols, triols … polyols (e.g. sugar alcohols), thus a general classification should not neglect these options. As a result, when discussing mixtures the classes used are alkanes, from alkanes derived alcohols (alkanols) incl. sugar alcohols, carboxylic acids (fatty acids), amines, amides, and esters.

Macro-molecules, when talking about PCM, refer to polymers (Figure 8); they have hundreds to thousands of the same building blocks. Due to their large chain length polymers have very high viscosity in the liquid phase. It is not uncommon that they only change shape under a larger force, unlike liquids, and do not regain the initial shape if an applied force is removed, unlike solids. Such behavior is called plastic, specifically here thermoplastic. Polymers with that behavior are therefore called thermoplastics. Their phase change is precisely solid-plastic. Polymers also allow crosslinking the molecules by bonds; if done only at large distance they become elastomers, meaning they behave elastic all time, like a solid. If crosslinking is just at large distances the intermediate molecule parts can behave almost unaltered. While crosslinking causes a significant difference in the phase change behavior to solid-solid it is however a small change in the composition. It is also possible to attach the molecules that act as PCM at one end to the chain of a different molecule; this acts as backbone, allows them to loosen interaction along their molecules, but not completely. The backbone can be a polymer, a molecule of smaller size, and actually even attachment on a surface. The choice here for further classification is the material class, e.g. polyethylene, to be similar to the classification elsewhere, but also as classification to thermoplastics etc. is here not relevant; actually, it is even confusing when talking about the possibilities of mixtures. It is thus not shown in Figure 8, but if of specific interest it can be used for an individual classification.

Salts (Figure 8) are composed of ions, which might be formed by atoms or by small to larger molecules. This allows the formation of salts of different complexity, both ions from atoms have e.g. NaCl and LiF, one from a small molecule e.g. $NaNO_3$ and Na_2CO_3, both from a small molecule e.g. NH_4NO_3, and both ions from larger molecules e.g. $C_3H_5N_2^+CH_3SO_3^-$ (Matuszek et al. [16]). The complex ones often have lower phase change temperature, and due to the phase change solid-liquid are thus called ionic liquids.

3.3.2. Non-Pure Substances, Meaning Mixtures

Pure substances are elements, or chemical compounds which are composed of two or more elements in integer proportions, e.g. in H_2O being H:O as 2:1. Origin of the integer proportions are primary bonds: molecules have covalent bonds, salts have ionic bonds, built by electron sharing respectively transfer. Due to their fixed composition, pure substances have well defined physical and chemical properties, e.g. melting and boiling point. In contrast, non-pure substances are mixtures that have variable composition, thus variable physical and chemical properties. Substances combined in a mixture are called component (Atkins [10]); the ratio states the composition. Origin of possible variable composition, instead fixed, is a bonding that is neither covalent nor ionic; e.g. metal - metal mixtures (called alloys, metallic bond), water - salt mixtures (permanent dipole - ion), water - alcohol mixtures (permanent dipole - permanent dipole), water - O_2 mixtures (permanent dipole - induced dipole), and alkane - alkane mixtures (induced dipole - induced dipole). Despite having overall variable composition, there is still the possibility of specific proportions; origin is a geometric arrangement of the constituents. An example are salt hydrates, where one of the salt ions is surrounded by a specific number of water molecules.

Figure 9 shows a phase diagram (schematic) of H_2O - $CaCl_2$ mixtures, for a wide composition range. There are several salt hydrates: $CaCl_2{\cdot}2H_2O$, $CaCl_2{\cdot}4H_2O$, and $CaCl_2{\cdot}6H_2O$. At about 30wt.% the composition is eutectic; the liquid solidifies at a lowest temperature, here to solid ice and $CaCl_2{\cdot}6H_2O$. Eutectic transitions (at the corresponding composition) are between a homogeneous liquid and two or more solid phases; they show a phase change temperature, not a phase change temperature range, and typically solidification without phase separation. They are desirable, however other transition can also be useful. Regarding classification several things are important. Being a mixture, the phase change temperature and enthalpy varies with composition, and accordingly several compositions might be useful as PCM, here pure H_2O, the salt hydrate $CaCl_2{\cdot}6H_2O$ (sometimes modified), and a eutectic H_2O - $CaCl_2$ mixture. The type of phase transition can be congruent, incongruent, or semicongruent, and mixtures can also be homogeneous or inhomogeneous (e.g. if not congruent). None of these properties can be generalized. Thus, if two components, e.g. H_2O and $CaCl_2$ can be mixed, the outcome depends on the mixing ratio and depending on the individual case can be anything from useful as PCM to useless.

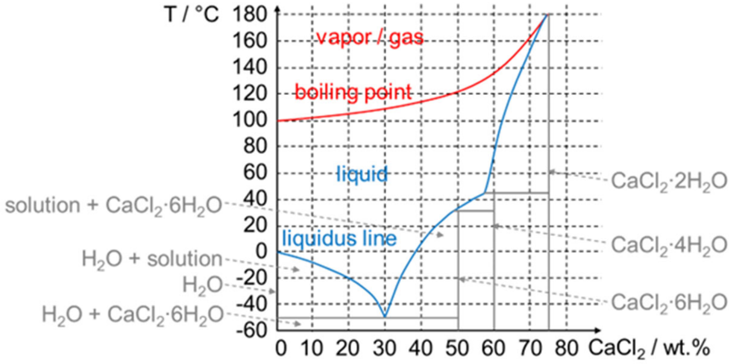

Figure 9. Phase diagram (schematic) of H_2O - $CaCl_2$ mixtures in a wide composition range.

With a focus that is development-oriented towards new PCM, to expand the choice of materials, the first, crucial question is what can be mixed? Then what has been mixed, and what was the outcome?

With regard to the question what can be mixed the theoretical background allows to have expectations. To form a mixture, atoms or molecules of the components to be mixed must loosen their bonds, and form new bonds with those of other components, e.g. in water-salt mixtures the water bonds (permanent dipole) and the salt bonds (ion) are loosened and new bonds are then formed (permanent dipole - ion). There is one exception: inclusion compounds, e.g. gas hydrates; here the better energetic stability does not come from new bonds but from energetic optimization of the water by a modified crystal cage. Important is also that molecules can have more than one type of bond, e.g. alkanols and fatty acids have molecule parts with a permanent dipole at their functional group as well as induced dipole at the rest. Consequently, looking at the atoms and molecules a first expectation what can be mixed can be justified. Classification schemes found in literature (Figure 3, 4, and 5) have used organic, inorganic, and mixtures thereof for classification, however as explained before organic and inorganic are not useful. As a consequence, here the previously identified subclasses are used: from elements metals and semi-metals, from molecules water, alkanes, from alkanes derived alkanols incl. sugar alcohols, carboxylic acids (fatty acids), amines, amides, and esters, the polymers, and from salts simple and complex ones.

Binary mixtures, meaning mixtures of two components, are by far the most common ones in PCM R&D. To give an overview of the material options for the search for new, suitable PCM candidates, including already established PCMs, classification of binary mixtures is essential. An overview shows Figure 10, splitting binary mixtures into ones of the same subclass and those of different subclasses.

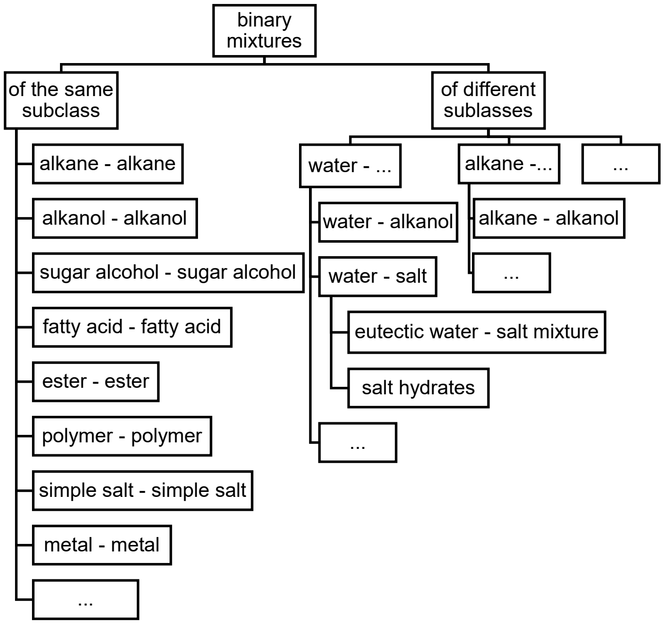

Figure 10. Classification of binary mixtures as PCM.

Binary mixtures of the same subclass, e.g. alkane - alkane binary mixtures, are straight forward. Generally, a positive outcome can be expected for mixing as both components have the same bond type, as well as suitability as PCM because the subclasses themselves have already shown to be promising. A review of available literature showed that this has been already experimentally verified for alkane - alkane binary mixtures (e.g. Mondieig et al. [17], Gunasekara [18]), alkanol - alkanol binary mixtures (e.g. Gunasekara [18]), sugar alcohol - sugar alcohol binary mixtures (e.g. Palomo Del Barrio et al. [19], Gunasekara [18]), fatty acid - fatty acid binary mixtures (e.g. Bidiyasar et al. [20], Zhou et al. [21]), ester - ester binary mixtures (e.g. Rubio-Pérez et al. [22]), polymer - polymer binary mixtures (e.g. Stewart et al. [23]), simple salt - simple salt binary mixtures (e.g. Gunasekara [18], Maldonado et al. [24]), and metal - metal binary mixtures (e.g. Gunasekara [18], Maldonado et al. [24]).

Binary mixtures of different subclass can be classified in different ways. Here the choice is made to start with mixtures where water is a major component, as water significantly reduces the cost of mixtures. Water - alkanol binary mixtures exist, and potential PCM are identified (e.g. Rathgeber et al. [25]). Water - simple salt binary mixtures are extensively used as PCM, eutectics at temperatures below zero (e.g. Yang et al. [26]), and salt hydrates above zero (e.g. Gunasekara [18] and many other authors). For alkanes, potential PCM were found in alkane - alkanol binary mixtures (e.g. Rathgeber et al. [27]), alkane - fatty acid binary mixtures (e.g. Rathgeber et al. [27]), as well as alkane - ester binary mixtures (e.g. Rubio-Pérez et al. [22]). Potential PCM can also be found in alkanol - fatty acid binary mixtures (e.g. Rathgeber et al. [27]), as well as fatty acid - ester binary mixtures (e.g. Rubio-Pérez et al. [22]). Binary mixtures between metals and semi-metals also exist, and were discussed as PCM (SERI [28]).

The previous examples show that already the binary mixtures where potential PCM were found cannot be displayed together with the others in a single classification scheme anymore. A comprehensive coverage requires a classification only for binary mixtures.

For ternary mixtures, similar as for binary mixtures, all three components can be from the same subclass (e.g. alkane - alkane - alkane ternary mixture), from two different ones (e.g. water - salt - salt ternary mixture), or from three different ones (e.g. water - salt - alkanol ternary mixture). Taking into account the number of different alkanes, alkanols etc., the number of binary or ternary combinations is already uncountable. On top comes that each component can be present at various concentrations in the mixture, thus lead to several new PCMs. For example, for water - salt binary mixtures it is common that one or several salt hydrates exist, and a eutectic of water and the hydrate with highest number of water molecules at subzero temperatures. Also, in ternary mixtures it is not uncommon that one component is rather an additive of minor amount, with the goal to only slightly improve the thermal performance of the binary system of main components.

Figure 11 finally summarizes the classification of PCM as suggested here.

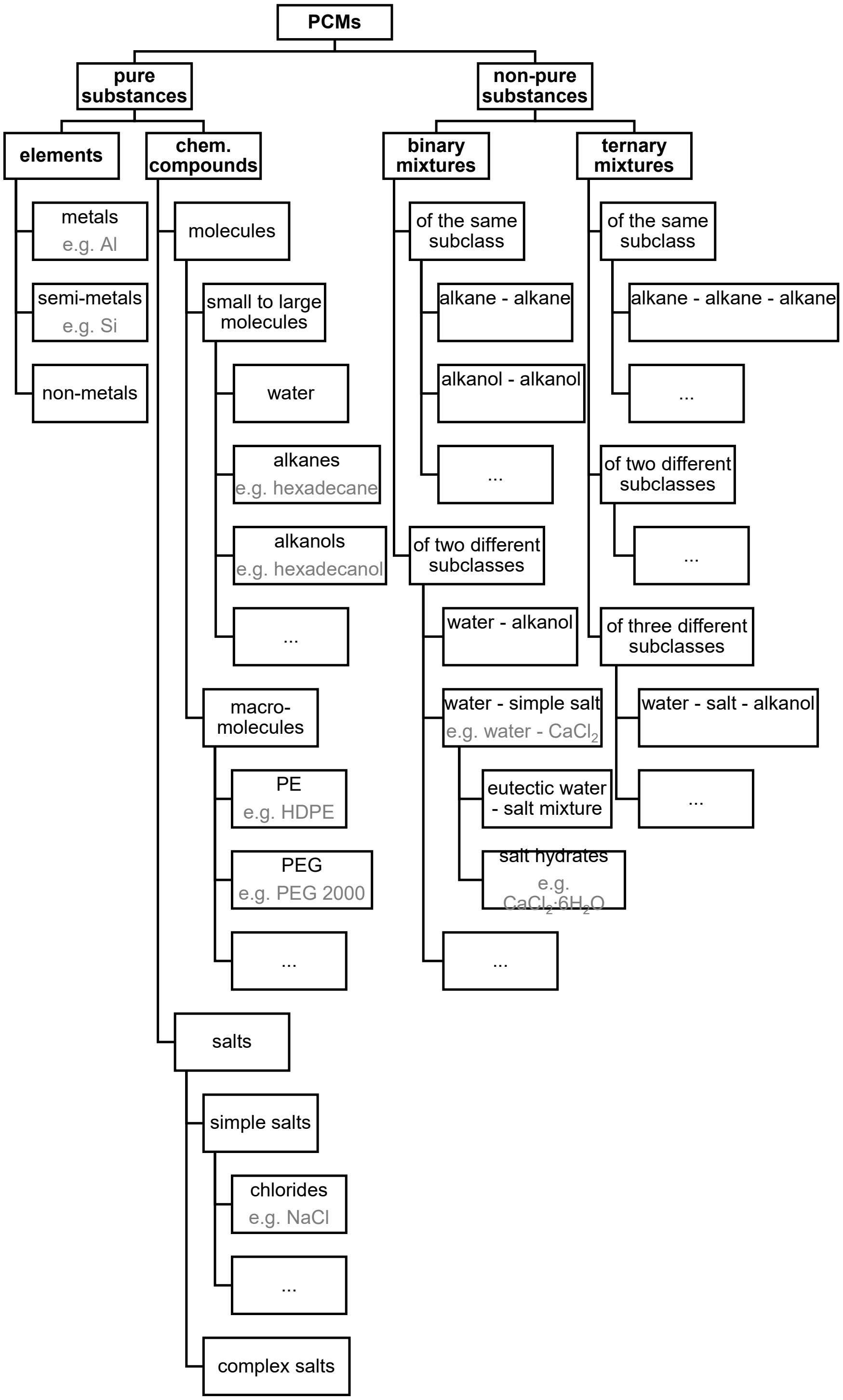

Figure 11. Complete classification to give an overview of the material options for the search for new, suitable PCM candidates, including already established PCMs.

4. Summary and Conclusions

With a growing number of PCMs and new, suitable PCM candidates, an overview is not only important, but also increasingly complex. Classification of PCMs thus changed significantly in the past decades. A review of classification of PCMs from recent years, performed here, shows that not only different classification criteria are used, but more important that they are often mixed, used inconsistently, and even without a clear goal. Focusing on the main goal of current classification schemes identified here, to give an overview of the material options for the search for new, suitable PCM candidates, including already established PCMs, then a consistent classification was developed in several consecutive steps. First, the general options for classification criteria were reviewed, and then the appropriate ones selected. Based on them a new, revised PCM classification was suggested (Figure 11). It is specifically detailed with regard to mixtures. For binary mixtures it is based on a literature review performed, and is extending current classifications. The new classification has a clear goal and related focus, it is clearly structured, and has correct terms. This becomes clear by comparing the general features of common classification (Figure 3, 4, and 5) with the newly developed (Figure 11). Specifically worth mentioning is removing the term eutectic which is commonly falsely used for mixture, and the widespread use of organic and inorganic which nowadays with the many material classes used as PCM does not give any specific information any more, often actually is even implying a wrong generalization of properties.

Clearly mentioning mixtures, identifying subclasses, and important examples, is crucial in two ways. First, mixtures allow the use of cheaper and / or more abundant components, thus allowing cost reduction, something that is specifically obvious in the salt hydrates, the eutectic water-salt mixtures, and others. Second, mixtures increase the number of available T_{pc} and thereby the choice of PCMs. Figure 12 shows this, by the melting temperatures of 15 pure saturated fatty acid PCMs, and further on the additional (predicted) melting temperatures already available from their binary eutectic mixtures. Also, mixtures typically have lower phase transition temperatures than their components, thus that mixtures can increase the range of phase transition temperatures with in a class to lower temperatures.

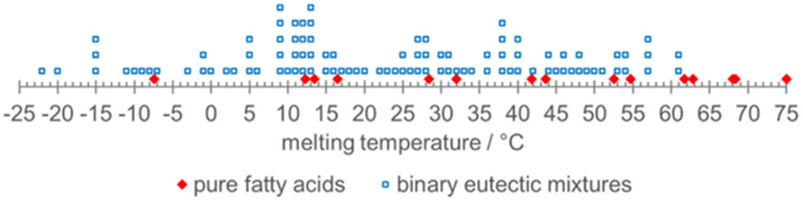

Figure 12. Melting temperatures of 15 pure saturated fatty acids and calculated ones for their binary eutectic mixtures (data source: Kahwaji and White [29,30]).

The classification by pure substances and non-pure substances, meaning mixtures, which is done here on the top classification level (Figure 11), also correlates with typical cases where classification is used. Important R&D issues for pure substances, which are also the components in mixtures, are the sources (bio-based, fossil-based, food-based, waste-based …) and related if only extracted from the source or if moreover modified by a chemical process. The latter can be expected to become a new R&D topic. First publications in that direction are already available, e.g. Soodoo et al. [31] discuss properties of several organic PCM classes (fatty alcohols, fatty acids, esters ...) that can be derived from triglycerols, which are a main component of vegetable oils, and even earlier, Gallart-Sirvent et al. [32] have derived fatty acids from non-edible animal fat waste, and also investigated some of their salts as potential PCM. The latter is also an example of chemical modification of a substance that already is suitable as PCM to get another one that is also suitable. Crosslinking and grafting also are connected to this R&D field. Important R&D issues regarding mixtures are determining what can be mixed and the phase diagrams, predicting T_{pc} and $\Delta_{pc}h$, actual characterization, and if needed, optimizing the phase transition behavior to become congruent melting by additives. Thus, classification is tightly connected with R&D fields.

Despite significant improvements some unsatisfactory issues remain, specifically regarding terms used. Still common is the term paraffin, while really meant are alkanes, specifically linear saturated alkanes. In a similar manner, it is common to classify by the functional group, e.g. alcohols, carboxylic acid etc. But usually meant are those derived from linear saturated alkanes with the functional group at the end. This is not critical in a general classification, but it should be considered if attempting a detailed one, e.g. distinguishing linear and non-linear saturated alkanes, specifying primary, secondary alcohols etc. Further on, many mixtures with water have a eutectic composition that is suitable as subzero PCM, e.g. water-salt mixtures (Figure 9) or water-alkanol mixtures. To say then e.g. eutectic H_2O - $CaCl_2$ mixture is correct, but other eutectics can be present in the phase diagram thus that the term is not fully precise. Nevertheless, currently no better one exists.

Last, but not least, it must be stressed again that the classification suggested in Figure 11 is for the goal to give an overview of the material options for the search for new, suitable PCM candidates, including already established PCM. For other goals, or other focus, classification can and should be done different. Nevertheless, the options for classification criteria identified in section 3.1 (Table 1) give a guidance.

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