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**Phase changing slurries in cooling
and cold supply networks**

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Phase Changing Slurries in cooling and cold supply networks

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1 Introduction

Conventional cold supply networks are using water or brine as heat transfer fluids. The storing of cold is often implemented by hydraulic buffers or by ice storage systems. Due to small temperature differences between forward flow and return flow, the volumetric flow rate of cold water or brine networks are very high and the cold capacity of hydraulic buffers are very low. Conventional ice storage systems have got a limited thermal power, because these systems have got an additional heat transfer in a heat exchanger and ice is a very good heat insulator.

Therefore Phase Changing Slurries PCS with a higher heat capacity have been discussed in the last years. The PCS are using latent and sensitive heat. They are suitable as cold transfer fluids and store cold easily by hydraulic buffers. At present, there are mainly three PCS proposed for cooling and cold supply networks and applications: Ice-slurries as two-phase single component system and paraffin/water emulsion or encapsulated paraffin/water suspension as two-phase binary mixture. Generally, Ice-slurries are more suitable for application in the temperature range under 0 °C and paraffin/water for the temperature range above 0 °C.

Fraunhofer UMSICHT is investigating PCS systems in view of their possible application. Paraffin/water emulsion and encapsulated paraffin/water suspension are discussed as heat transfer fluid as an alternative to cold water. Tetradecane was chosen as paraffin for these fluids because of its melting point of 5 °C. Ice-slurries could be used as alternative to brine or as cold storage fluid for a mobile cold supply.

2 Material properties of PCS

2.1 Heat Transfer capacity of PCS

PCS pass a phase changing process during the absorption and release of heat. The phase changing process permits the PCS to use, additional to the sensitive heat of a temperature difference, also the melting heat during the phase changing process. Thus increase the heat capacity of the fluid and improves the heat transfer capacity of cold supply networks. The necessary volumetric flow rate in the cold supply network can be reduced. The reduced volumetric flow rate permits to reduce pump power and pipe dimension, which lower operating and investment costs. The storage capacities of conventional energy buffers can be increased.

The figure 1 shows the volumetric heat capacity of a tetradecane/water mixture compared with water. The heat transfer capacity is rising with increasing weight percent of paraffin. At a concentration of 12 weight percent, the heat transfer capacity is about two times higher than only water. At a concentration of 25 weight percent, the heat transfer capacity is about three times higher.

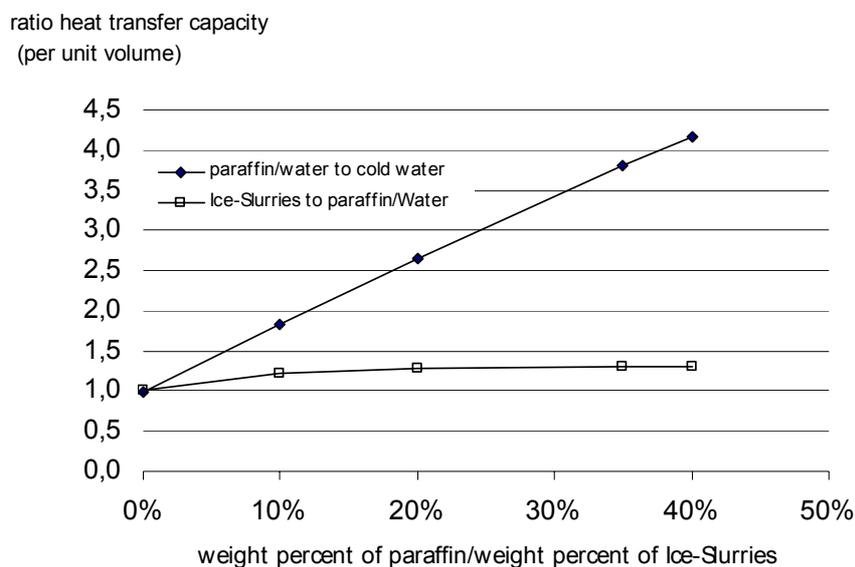


Figure 1: heat transfer capacity rate of tetradecane/water and ice-slurries

Figure 1 shows also the heat transfer capacity of a tetradecane/water mixture compared to ice slurries. The heat transfer capacity of ice-slurries is bigger than the heat transfer capacity of the tetradecane/water mixture due to the high amount of melting heat of ice. An advantage of paraffin/water mixtures are, that the melting point of the mixture can be adjusted by mixing different paraffins. The temperature range of 0-18 °C can be covered for example by a mixture of tetradecane and hexadecane due to He [i]. The enthalpy of the melting process for pure paraffin's is nearly constant between 218-240 kJ/kg. The enthalpies of paraffin mixture can descent to 150 kJ/kg.

2.2 Two phase binary mixtures

Two two-phase binary mixtures have been investigated: tetradecane/water emulsion and encapsulated tetradecane/water suspension. Both fluids have been tested in a small test rig in laboratory scale. The fluids have been cooled down and afterwards

warmed up again by a heat exchanger. Figure 2 shows the temperature change and cold power output during the tests.

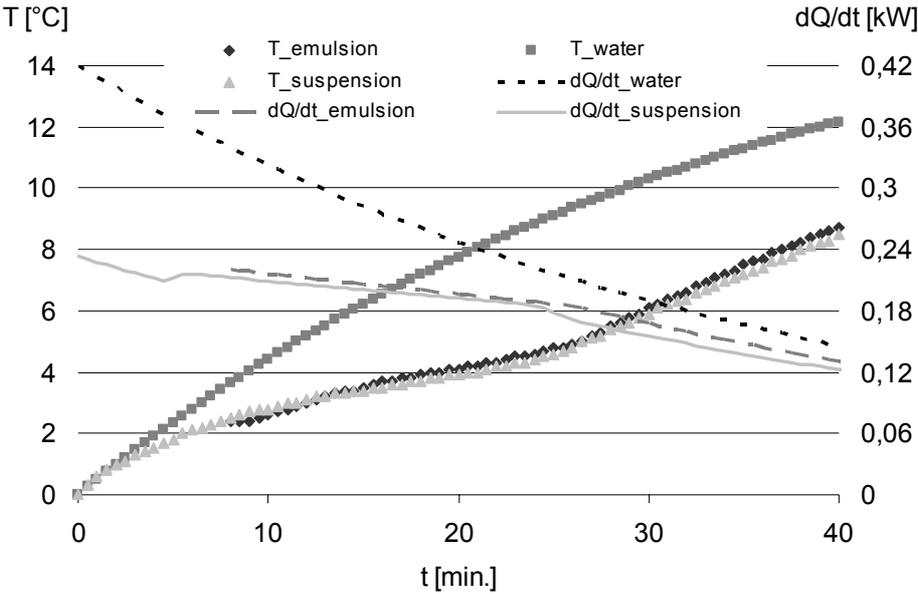


Figure 2: temperature curve of the buffer and cold power output

The temperature curves of the emulsion and suspension are less rising than the temperature curve of water. Each of both curves has got two bend points at about 2 °C and at about 4.5 °C. These bend points identify the start and the end of the phase changing process. The cold power output of the heat exchanger is bigger with water as heat transfer fluid than with the PCS-fluids. This indicates that the heat transfer of water is better than the heat transfer of the PCS-fluids. The Table 1 shows parameter which could be derived from the tests.

Table 1: parameters of the tests

Parameter	Emulsion	Suspension
Concentration of paraffin	20 %	14 %
Phase changing	41 %	80 %
$C_p + r$	9.71 kJ/kg/K	11.45 kJ/kg/K
ΔT during phase changing	2.6 K	2.3 K

The heat capacities of the emulsion and suspension were 9.71 kJ/kg/k and 11.45 kJ/kg/K. A total freezing of the fluids was not achieved during the tests. The reason is supposed to be sub-cooling effects. The concentration of the paraffin can be still raised. According to Inaba [ii] emulsion with 40 weight percent should be possible.

The viscosity and shear rates of the two-phase binary mixtures have been measured by a rotary viscosimeter. Figure 3 shows the shear stress versus the shear rate of the investigated tetradecane/water emulsion. The paraffin was liquid while the viscosity measurement.

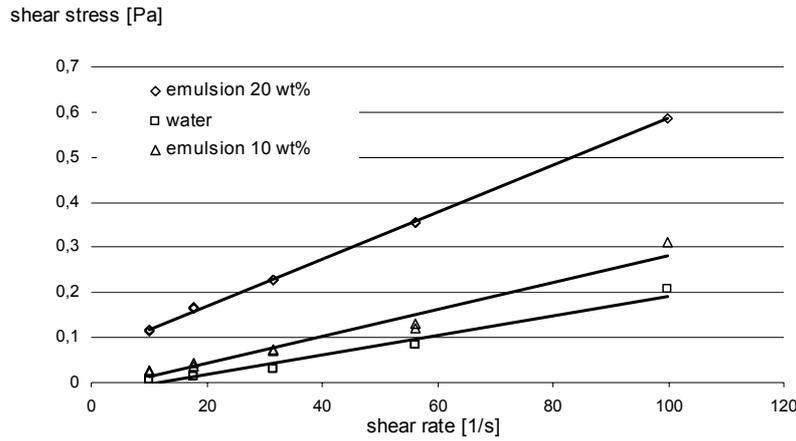


Figure 3: shear stress versus shear rate for a tetradecane/water emulsion

The emulsion shows Newtonian behaviour in the investigated concentration range of 10 to 20 weights percent. Figure 4 shows the shear stress versus the shear rate of the encapsulated tetradecane suspension. The suspension shows the behaviour of an Ostwald-de-Waele-fluid.

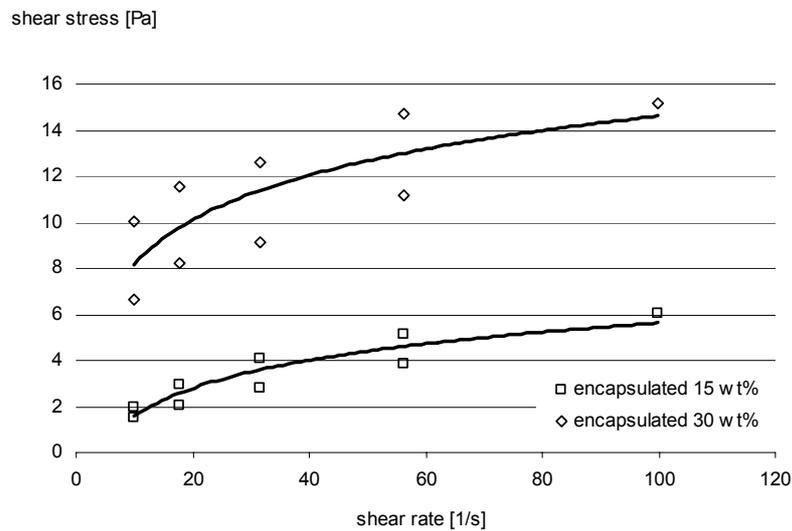


Figure 4: shear stress versus shear rate for encapsulated tetradecane suspension

The viscosity of the emulsion is 2 to 8 times higher than the viscosity of water depending of the concentration of tetradecane. The viscosity of the encapsulated tetradecane suspension is 120 – 550 times higher. The rheological properties of the investigated two-phase binary mixture can be compared to the rheological properties of fine dispersion. The effective viscosity can be calculated according to Vand [iii] with the following equation (1).

$$\eta = \eta_w \cdot (A + B \cdot x + C \cdot x^2) \quad (1)$$

The variable x is the concentration of the fluid and η_w the dynamic viscosity of water. The parameter A, B and C are given in Table 2:

Table 2: Parameter to calculate the effective viscosity

Fluid	A	B	C
Emulsion	1	2	50
Suspension	1	228	6211

The Figure 5 shows the calculated specific pressure drop for water, tetradecane/water emulsion and encapsulated tetradecane/water suspension.

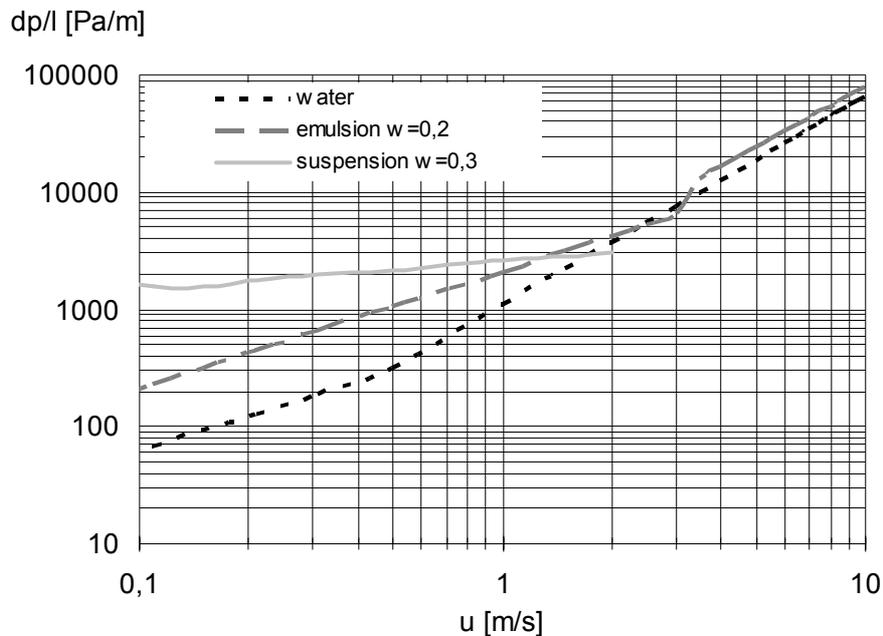


Figure 5: pressure drop versus flow velocity

The paraffin/water emulsion and paraffin/water suspension cause bigger pressure drops than water in the range of laminar flow. The pressure drop curves amalgamate in the turbulent flow range. The behaviour of suspension in the turbulent flow range must be still further investigated.

2.3 Two phase single component

Figure 6 shows the temperature curve and the cold capacity which can be obtained during the melting process of Ice-slurries.

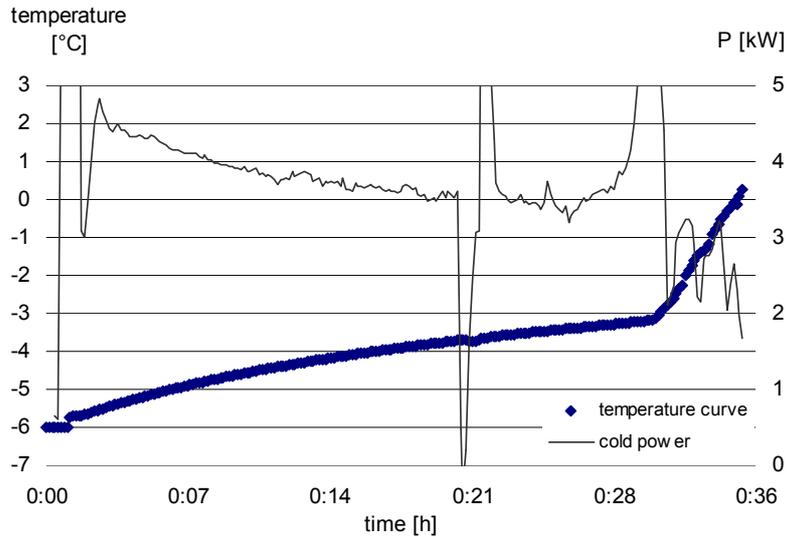


Figure 6: temperature curve and cold power during the melting process of Ice-Slurries

The investigated Ice-slurries were adjusted for a melting point of $-3\text{ }^{\circ}\text{C}$ and had an ice concentration of about 40 weight % at the beginning of the test. Due to the fact that the melting process of Ice-Slurries takes place continually with rising of the temperature, there is only one bend point which indicates the end of the melting process. The cold power drops almost 30 % with the end of the melting process.

The rheological behaviour of Ice-Slurries can be described by the Casson Model according to Dötsch [iv]. The Casson model describes a flow behavior with a shear thinning effect and a bingham-plastic influence expressed by equation 2. The Casson parameter τ_C characterizes the bingham influence and η_C characterizes the shear thinning viscosity. In the case that τ_C is going against zero, the bingham plastic effect disappears and the Casson model changes to the Newtonian model.

$$\tau = \left(\sqrt{\tau_C} + \sqrt{\eta_C \cdot \dot{\gamma}} \right)^2 \quad (2)$$

The Casson parameter τ_C and η_C depends mainly on ice content Φ [Vol. %] and the viscosity of the ice free fluid phase η_{MP} (matrix phase). The correlation between τ_C , η_C and both ice share and viscosity of the ice free fluid phase is shown in figure 7.

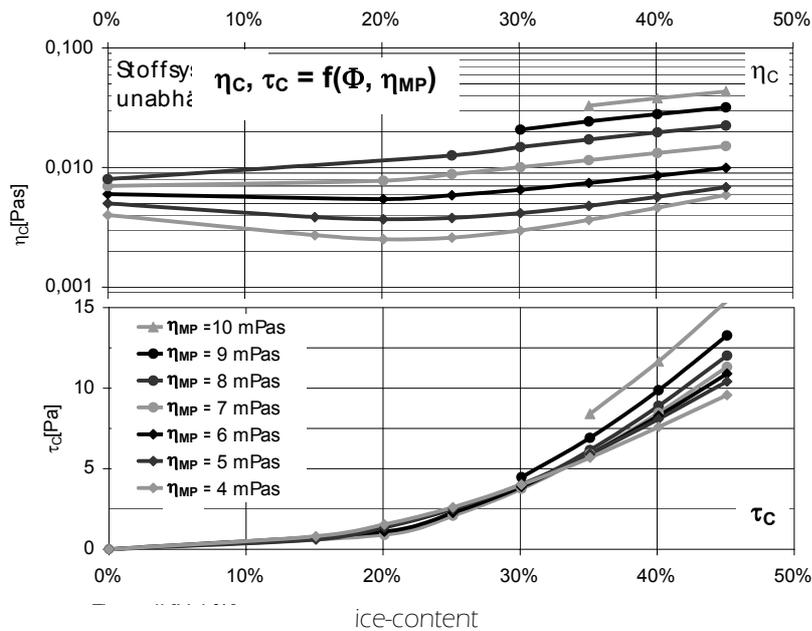


figure 7: Casson parameter τ_c and η_c in dependence of ice share Φ and viscosity of the ice free fluid phase η_{MP} (4-10 mPas)

Figure 8 shows the calculated specific pressure drop for ice-slurries. Different concentrations of ice have been considered.

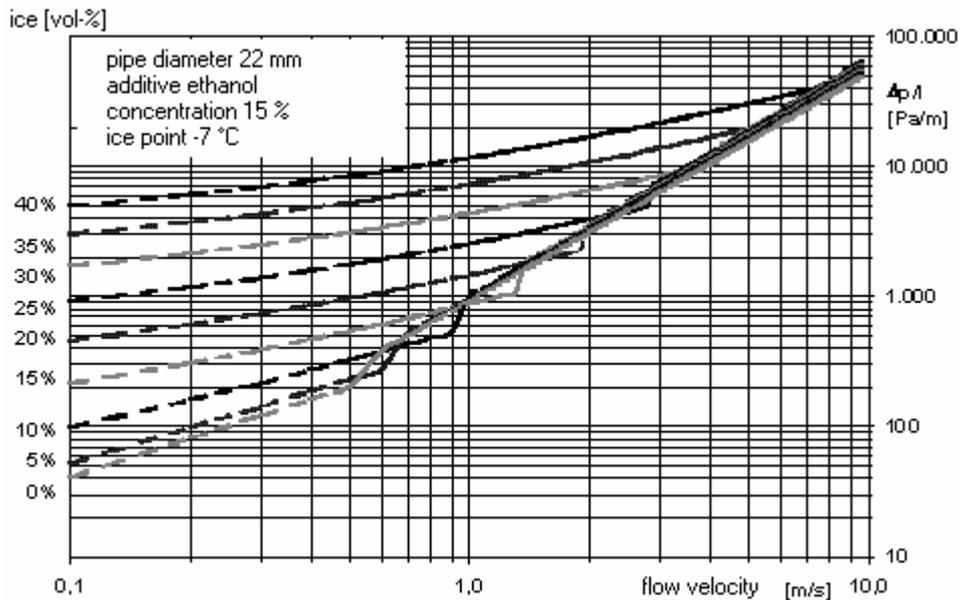


Figure 8: pressure drop versus flow velocity and varying concentration of additives

Ice-slurries with higher concentration of ice cause bigger pressure drops. Under turbulent flow conditions the pressure drop curves amalgamate and proceed with the same gradient.

3 Field of application

3.1 PCS in cold supply networks

The possibility of a cold supply based on PCS has been discussed under economical aspects. Table 3 shows the assumptions and results of a comparison between tetradecane/water mixtures, ice-slurries and cold water for a fictive cold supply network. The calculation takes into account the costs of the cold generation as well as the costs of the cold distribution. The cold capacity is 500 kW. The length of the distribution network was estimated with 600 m. The operating time is 1000 hours per year. The concentration of paraffin and ice-slurries are assumed with 20 % and tetradecane was used as paraffin. The concentration and the paraffin were chosen, because respective PCS could already be produced and have proven their applicability in preliminary experiment. But a higher concentration is aimed for future application as well as an adjustment of the melting point of the paraffin/water mixture by using a paraffin mixture.

	water	PCS-tetrad./water	Ice-Slurry	
cold power	500	500	500	kW
$T_{\text{evaporator}}$	5	2	-5	°C
$t_{\text{operating}}$	1000	1000	1000	h/a
COP	3.53	3.19	2.59	-
I_{chiller}	49,438.20	58,666.67	80,000.00	€
$I_{\text{auxiliaries}}$	49,438.20	58,666.67	80,000.00	€
<u>annuity</u>	0.119	0.119	0.119	1/a
p	1.06			-
t_{usage}	12			a
costs of electricity	0.07	0.07	0.07	€/kWh _{el}
auxiliary energy	0.04	0.04	0.04	kWh _{el} /kWh _{th}
maintenance	3,955.06	4,693.33	6,400.00	€/a
investment costs	11,793.68	13,995.17	19,084.32	€/a
operating costs	11,314.51	12,362.29	14,898.35	€/a
total generation costs	27,063.25	31,050.80	40,382.67	€/a
distribution work	50842	24412	10142	kWh/a
distr. operating costs	3,559.00 €	1,709.00 €	710.00 €	€/a
distr. invest. costs	11,685.0	7,680.0	7,511.0	€/a
<u>total distribution costs</u>	15,243.43	9,388.63	8,221.40	€/a
costs of cold supply	42,306.68	40,439.43	48,604.07	€/a
<u>specific costs</u>	0.085	0.081	0.097	€/kWh

Table 3: Economical comparison for a cold supply network

Because of the high heat transfer capacity of ice-slurries, ice-slurries have got the lowest distribution costs. The distribution costs of PCS-tetradecane/water are still lower than the distribution costs of water. The calculated distribution costs take the different rheological behaviour with the related higher pressure drops of the PCS into account. Due to the fact that the evaporator temperature of the refrigeration has to be lowered to produce ice-slurries or to freeze tetradecane, the COP of the refrigerator becomes worse and consequently the cold generation more expensive. The PCS-tetradecane/water can compensate the additional costs of the cold generation by the

costs reduction of the cold distribution, so that the PCS-tetradecane/water has got the lowest specific costs for the regarded cold supply. The costs reduction for the distribution of the ice-slurries can not compensate the additional costs of the cold generation, so that the ice-slurries solution is finally more expensive than the conventional cold water system. This calculation example also indicates that ice-slurries are more suitable as alternative for cold supply networks which operate normally with brine in the temperature range under 0°C. Additional costs for the cold generation, due to a worse COP, can not be considered in these systems. Under the above assumptions, a cold supply network based on brine would have operating costs of 4,700 €/a, which is still higher than the cold water network due to the worse heat capacity of brine and higher pressure drop in the network. Supposed the same investment costs for the brine system as for the cold water system, the total distribution costs are two times bigger than the total distribution costs of ice-slurries. Furthermore it must be mentioned here, that the improved heat capacity of the fluids also improves the heat storage capacity of the cold supply network. The resulting positive effects have not been taken into account in the above comparison.

Besides the economical aspects, there are also some technical aspects which must be considered. PCS are mixtures of different substances. Also ice-slurries contain additives. The use of these substances in supply networks demands system requirements according to the nature of the used substance. For example, paraffin is a solvent for rubber, so that seals of EPDM should not be used in cold supply networks based on paraffin/water mixtures. Viton can be used as alternative to EPDM. Pumps, instruments and other devices with viton as seal material are available on the market without problems. Another important point is the water endangering potential of the used substance. For example the additives sodium chloride, ethanol and propylene-glycol, which are used for ice slurries, belong to WEC 1 according the German Water Management Act. If the concentrations of a substance of WEC exceed a concentration of 3 % in mixture, the mixture is also considered to WEC 1. The paraffin tetradecane belongs to WEC 1. The used additives for a water/tetradecane emulsion are mainly detergents, which belong to WEC 2. The wall material of encapsulated tetradecane may belong to WEC 1 or WEC 2. If the concentration of a substance of WEC 2 in the mixture is smaller than 5 weight percent, the mixture is still considered to WEC 1. The concentration of additives in the investigated and here discussed fluids could be kept under the required values so that the fluids would be classified to WEC 1. In this context, it must be mentioned that conventional brines are also considered to WEC 1. Due to the classification of the PCS, respective safety measures have to be implemented. The necessary safety measures for a cold supply network with fluids of WEC 1 depend on its size and are shown in the following Table 4:

Volume of the system [m ³]	Measure
< 0.1	There are no special measures for the system
> 0.1 to 1	<ul style="list-style-type: none"> • tight surfaces with regard to the fluid • detention basins for the volume of fluid which could be emitted during a operating disorder without counteractions • supervision by a control room or regular tours of inspection
1-100	<ul style="list-style-type: none"> • tight surfaces with regard to the fluid • detention basins for the volume of fluid which could be emitted before counteractions have an effect • supervision by self operating alarm annunciation systems in combination of a control room or regular tours of inspection
100 – 1000	<ul style="list-style-type: none"> • tight surfaces with regard to the fluid • detention basins for the volume of fluid which could be emitted before counteractions have an effect • supervision by self operating alarm annunciation systems in combination of a control room or regular tours of inspection • alarms and measurements to prevent water pollution in accordance with facilities which are involved in the measurements

Table 4: safety measures according to the German legislation

The disposal or a possible recycling of the fluids depends of the components of the fluids and the possibility to separate the components. Generally, the investigated fluids are not considered as hazardous substance. Tetradecane could be recovered but has to be separated from the fluid. There are recycling plants which are specialised in recycling of emulsion. The costs of the recycling of emulsion is about 180 €/t. The emulsion would have the European waste code EWC 120 109. The encapsulated tetradecane/water suspension can be filtered to separate the water from the encapsulated tetradecane. The separation of the capsule material from tetradecane would be very expenditure so that the incineration of the complete encapsulated tetradecane would be a convenient way of disposal.

3.2 Ice-slurries for mobile cold supply

A new concept of an innovative cold supply is mobile cooling */M*. Mobile cooling is using waste heat from industry processes, from the power generation or excess heat of district heating in the summer. The idea is to use the waste heat to produce ice-slurries by a thermal refrigeration process as for example ammonia absorption chiller. The ice-slurries are stored in container and transported to the cold consumer by trucks. Cold consumer could be offices or super markets. The container has got a volume of 25 m³ and the ice concentration may reach 55 %. Such a container would have a cold capacity of 1.600 kWh with a high discharge power.

The concept has been assessed within a feasibility study. A basic fictive example was defined. A waste heat source of 2 MW_{th} is used to produce ice-slurries by an ammonia absorption chiller with a cold capacity of 1 MW_{th}. Assumed that the absorption chiller is operating 24 h, the cold capacity is enough to provide the necessary cold work for 8 consumer with a cold work demand of 2880 kWh/d relating to a cold power of 180 kW. Two containers are foreseen for one cold consumer, who is located in a distance of max. 15 km. This example is economically compared to a conventional cooling system in Table 5.

	mobile cooling	conventional cooling	
yearly demanded cold work	3049	3049	MWh/a
number of chiller	1	8	
cold power of the chiller	1000	480	kW
operating time (full load)	3064	794	
electricity price	10	10	ct/kWh
heat energy price	10	10	€/MWh
water and waste water price	2		€/m ³
transport costs	0.027		€/kWh
payout time	15	15	a
interests	8	8	%
price increase	3	3	%
factor of annuity	1.19	1.19	
investment costs	2017	1901	T€
investment costs per year	235	222	T€/a
operating costs per year	371	318	T€/a
specific costs	198.84	177.24	€/MWh

Table 5: Economical comparison of mobile cooling to a conventional cooling system

Although the specific costs of mobile cooling are little higher than the specific costs of a conventional cold supply, this example shows that mobile cooling may compete to the conventional technique. A sensitivity analysis was made with the objective to ascertain the influence of the input variable and assess the potential of mobile cooling. Table 6 shows the results of the sensitivity analysis.

input variable	old value	new value	unit	costs mobile	costs conventional	
				cooling	cooling	
transport distance	15	5	km	178.74	177.24	€/MWh
transport distance	15	20	km	208.89	177.24	€/MWh
payout time	15	20	a	194.52	173.21	€/MWh
payout time	15	10	a	214.16	191.97	€/MWh
electricity price	10	3	ct/kWh	198.7	137.92	€/MWh
electricity price	10	20	ct/kWh	199.04	233.41	€/MWh
interest	8	5	%	187.1	166.04	€/MWh
price increase	3	0	%	181.06	160.64	€/MWh

Table 6: Sensitivity analysis of mobile cooling

The sensitivity analysis indicates in particular the importance of the transport distance and the electricity price. The cost-effectiveness may be increased under different condition.

4 Resume and Prospects

The investigated PCS-fluids are suitable as alternatives to conventional heat transport fluids. The higher heat capacity of these fluids is promising lower operating and investment costs. Paraffin/water fluids can be used for application in the temperature range over 0 °C. The temperature range under 0 °C can be covered by ice-slurries. Contingent higher pressure drops have to be considered for the design of respective networks. The investigated emulsion has shown almost Newtonian behaviour. The suspension has shown an Ostwald-de-Waele behaviour. Ice-slurries may have a Newtonian, Ostwald-de-Waele and Bingham behaviour depending on their composition and flow conditions. The flow characteristics of ice-slurries can be well described by the Casson Model.

A future application of PCS in cold supply networks seems to be feasible under technical and environmental aspects. A first calculation with tetradecane/water PCS shows economical benefits in competition to cold water. Ice slurries systems are expected to be more profitable than brine systems. Furthermore a new mobile cold supply on base of ice slurries is discussed.

Currently Fraunhofer UMSICHT is investigating PCS with the objective to optimize their composition and improve their properties in research project. Additionally application-oriented aspects are investigated in test rigs. The research project is funded by the German Bundesministerium für Wirtschaft und Arbeit.

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- i He, B., Gustafsson, E. and Setterwall, F.: Tetradecane and Hexadecane binary mixtures as Phase Change Materials (PCMs) for Cool Storage in District Cooling Systems. *Energy* 24 pp.1015 – 1028, 1999
 - ii Inaba Hideo, Shin-ichi Morita, Shigeru Nozu: Fundamentals Study of Cold Heat-Storage System of O/W-Type Emulsion having cold latent-heat-dispersion material. Part 1. *Heat Transfer Japanese Research*. Vol. 23, Nr. 3, S. 292. 1994
 - iii Vand, V.: Viscosity of Solutions and Suspensions I, II, III. *The Journal of Physical and Colloid Chemistry*, Bd. 52, 277-321. 1984
 - iv Doetsch, C.: Experimentelle Untersuchungen und Modellierung des rheologischen Verhaltens von Ice-Slurries, Fraunhofer IRB Verlag, PhD Thesis Oktober 2001
 - v Beier, C., Dr. Dötsch, Ch., Heinz, et. al.: Vorstudie: Mobile Kältelieferung. Abschlussbericht. Projektträger Jülich (PTJ-ERG). Forschungseinrichtung: Fraunhofer UMSICHT Oberhausen. 2005