Corrosive effects of salt hydrate Phase Change Materials used with aluminium and copper

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Phase Change Materials (PCMs) provide good potential for reducing energy consumption in thermal energy storage systems. The characteristics of two PCMs suitable for energy storage in air-conditioning and ventilation systems are discussed outlining their advantages and disadvantages. One of the main disadvantages of PCMs lie in their corrosive nature when in direct contact with metal components such as piping or housings. This research work reports on the corrosion rates of two materials commonly used in heat exchangers in the air conditioning industry along with their metallographic examination following corrosion tests. The materials tested were aluminum(Al) and copper (Cu) flat sections. The corrosion tests were carried out to the American ASTM G1 standard. The experimental work initially consisted of immersing aluminum and copper in the PCM materials. Following this, both aluminium and copper were immersed in the PCMs in the same container. From these experiments, the corrosion rates were determined. The effects of corrosion on aluminum and copper are presented and discussed along with recommendations for Hydrated salt PCMs use in ventilation heat exchanger equipment. Novel ways of preventing corrosion of copper and aluminum by these PCM materials are also presented. These include conductive polymer coatings, organic coatings and sacrificial methods.

1.   INTRODUCTION

This paper sets out the background and latest literature research on the subject of PCMs and corrosion. It is proposed to use the PCM as a thermal storage medium for conventional air conditioning heat exchangers. For successful application, the PCM must melt at approximately the supply air temperature of 18°C. There are currently two types of commercially available Hydrated salt PCMs available, and they will be examined for this purpose. Their characteristics and corrosion affects on two types of metals commonly found in such heat exchangers will be examined. Aluminium and copper are chosen as the reference metals, because they are most indicative of the current 'state of the art' heat exchanger materials. The methodology adapted to assess for corrosion is detailed, and the specific corrosive characteristics of two reference PCMs is then outlined. The results are then summarised and discussed, from which recommendations will be made regarding further research potential. Preventative measures are then outlined, and conclusions drawn for the use of hydrated salts in conventional aluminium and copper air conditioning heat exchangers.

2.   BACKGROUND TO PCMS AND CORROSION

Zalba *et al.* (2003) performed a comprehensive literature on thermal energy storage using PCMs; from which most references related to corrosion tests using salt hydrates involved testing using diluted salt hydrates, as typically used in the chemical industry. Nine references are cited in the review, of which only two presented actual results, and were based on observation over experimental set-ups – none of which examined salt hydrates with a melting temperature of 18°C. Porisini (1988) however examined four commercially available salt hydrates of which two melted within close range: Na2SO4.1/2NaCl.10H20 (20°C) and NaOH.2.5H2O (15°C). And tested each for corrosion rate on stainless steel, carbon steel, aluminium alloys, and copper. Following thermal cycling tests, Porisini concludes that stainless steel is the most corrosion resistant alloy to salt hydrates, however copper was shown to demonstrate a corrosion zone that did not increase after long periods of time. More recently, Cabeza *et al.* (2001; 2002) examined the corrosion resistance of five metals, including aluminium and copper, which were in contact with molten salt hydrates with melting temperatures of the order 0 to 10°C, 32 to 36°C, and 48 to 58°C. Table 1. summarises the corrosion rates for copper and aluminium in each case.

Table 1. Summary of corrosion affects from Salt Hydrate PCMs

Melting Temp. (°C); PCM	Reference Material	Corrosion	Corrosion rate (mg/cm^2y)		Reference		
48 to 58; Sodium Acetate	Aluminium	No Corrosion	i. ii.	0 0	Cabeza	*et*	*al.* (2002)
48 to 58; Sodium Acetate; Sodium thiosulfate	Copper	Severe corrosion through CuS	i. ii.	33.2 605	Cabeza	*et*	*al.* (2002)
-3; Sodium Carbonate;	Aluminium	Severe corrosion; not to be used	>1000		Cabeza	*et*	*al.* (2001a)
-3; Sodium Carbonate;	Copper	High corrosion: short term usage	13.9		Cabeza	*et*	*al.* (2001a)
32 to 36; sodium hydrogen (35) Calcuim chloride (32)	Aluminium	Severe corrosion; Pitting	Not available		Cabeza	*et*	*al.* (2001b)

Continued…

Melting Temp. (°C); PCM	Reference Material	Corrosion	Corrosion rate (mg/cm^2y)	Reference		
32 to 36; sodium hydrogen (35) Calcuim chloride (32)	Copper	Corrosion resistant; Corrosion resistant	Not available	Cabeza	*et*	*al.* (2001b)
32 to 36; sodium phosphate (35) Calcuim chloride (32)	Aluminium	Not recommened; Caution – short term use	Not available; 5.5	Cabeza	*et*	*al.* (2001c)
32 to 36; sodium hydrogen (35) Calcuim chloride (32)	Copper	Caution – short term use; Recommended	5-12; 0.4-5	Cabeza	*et*	*al.* (2001c)

Aluminium is shown to result in pitting when used with chlorides, the formation of Al(OH)3 after two weeks, demonstrating a low corrosion resistance; but is however resistant to Sodium acetate. Copper on the other hand is resistant to the calcium chlorides, but not so to the sodium acetates. Sodium sulphate composites (Na2SO4.10H2O + Na*Cl*) despite comprising of a sodium chloride mixture however is used as a PCM in an aluminium container, which is quoted to last some 20 years (Ure, 2003).

Corrosion of metals may be characterised as Pitting, Aqueous, Athmospheric, Hot corrosion, flow induced, SCC, Fretting (Schweitzer, 1983; Shreir, 1976). Galvanic corrosion can be characterised in terms of a standard hydrogen electrode, and the potential difference of the metal is measured. The galvanic series is based on immersion tests in seawater as an indication of the corrosion rate between metals and alloys in contact, in an electrolyte (the PCM for example). Metals at the active end will behave as an anode and corrode (Magnesium, Zinc, Aluminium) and the metals at the nobel end will behave as a cathod and be protected (Platinum, Silver, Copper) (CPC, 2002). Pitting corrosion is a localised form which produces holes. All metals are susceptical. To avoid pitting, metals should be isolated from stagnant solutions, protected from galvanic couples, and protective coatings should be non porous or crack free (Schweitzer, 1983)

Galvanic corrosion is a form of localised corrosion. When two dissimilar metals are coupled in the same electrolyte then extreme segregation will occur (Shreir, 1976). Iron and copper for example when placed in sodium chloride, and although oxygen reduction will occur on both metal surfaces, only the anodic iron metal will corrode. If both metals are of the same area therefore the iron will corrode twice the rate than if immersed in the solution without a connection to the copper. In aluminum, the iron al particles will facilitate intense hydrogen evolution leading to intense local corrosion therein. Electrons will flow from the iron to copper to support the differences in anodic and cathodic reaction rates. Since the potential of copper is less than aluminum, the corrosion rate will increase from the aluminum to the copper. Ideally the anode will be large (the aluminums surface area), and the cathode small (copper pipes), to prevent corrosion of the copper (CPC, 2002).

3. REFERENCE HEAT EXCHANGER AND PCM CHARACTERISTICS

The Heat Exchanger
A conventional heat pipe heat exchanger has been proposed as a viable low energy alternative to conventional cooling/heating coils as used in the air conditioning industry (Farrell, *et al.* 2002a). The heat exchanger consists of two chambers: one open to an air circulation system; the other sealed from the atmosphere and filled with a hydrated salt mix (PCM) to act as the heat sink for cooling, and the heat source for heating (Farrell *et al.* 2003). The size of the heat sink/source chamber is determined from the cooling/heating duration (Farrell, *et al.* 2002b). Both chambers are interconnected by the heat pipes, which are copper tubes, onto which aluminium fins are expanded. The copper pipes are thus plated with aluminium, but cracks, deformations may occur. The air side is expanded to fins at 3mm spacing, whereas the heat sink/source is at 6.25mm spacing to accommodate the PCM. The heat exchanger also incorporates horizontal plates between the fins at a vertical spacing of 50mm. The pates prevent stratification of the PCM sample 'PlusICE E17', which will become incongruent at depths greater than 50mm (Ure, 2003).

The Phase Change Materials

Table 2. PCM characteristics (Ure, 2003; Ulfvengren, 2003)

PCM	Melting temp.	Salt hydrate
PlusICE E17	17°C	Sodium Sulphate, Decahydrate, + Sodium Chloride
ClimSel C18	18°C	Sodiumacetate + additives

The E17 PCM is shipped in large 300L containers, whereas the ClimSel C18 in 1kg pouches. Upon initial visual examination, both materials appear as a white powder, with the ClimSel having a noticeable 'shimmer effect' from the 'metal infill' to improve the inherent low conductivity of the PCM.

Table 3. Properties of metals used

Element/metal	Aluminium (UNS A92024)	Copper (UNSC38600)
% Al	93.6	-
% Mg	1.5	-
% Mn	0.6	-
% Cu	4.5	99.9
Density (kg/m3)	2.78×10^{-3}	8.94×10^{-3}
Density (g/cm3)	2.78	8.94

The metal characteristics were determined from the American Society for Testing and Materials G1 UNS classification system (ASTM, 1996).

4.   EXPERIMENTAL CHARACTERISATION

Corrosion

Corrosion rate is generally expressed in terms of gravimetric analysis of mass loss of the material with respect to the initial mass (g). The corrosion rate is therefore the mass loss per square meter of surface and day (g/m2 d) (Cabeza *et al.* 2001). Owing to time constraints, an initial investigation over a 17 hour period was undertaken, and so the ASTM G1 standard for testing on an hourly basis was used. The experiment will assessed the corrosive nature of two PCMs with copper.

Apparatus:

Eight samples of copper and aluminium, Eight airtight glass containers; Electronic scales; Oven; Photographic Microscope (to 100 factor magnification); E17 PCM by EPS Ltd. UK, and C18 'ClimSel' PCM by Climator Sweden.

Methodology:
1.   All test samples of were cut, measured, and sanded for an even finish using grade P400 Silicon Carbite (SiC) water proof paper
2.   Each sample was cleansed of surface particles using a cloth
3.   The samples were then weighed

4.   A sample of each metal was then placed into each reference PCM: 2 samples of copper & aluminium separately, and two samples together, for both PCMs
5.   The reference samples of PCM were encapsulated from the air, and heated to fast melting rate temperature (70°C) for an hour
6.   The temperature was then lowered to 40°C for approximately 17hours
7.   The samples were then removed, and washed down using Nitric acid for the Aluminium, and hydro chloric acid with a 2:1 reagent water mix for the copper]
8.   The samples were placed into sperate beakers of water following immersion in the acids to minimise oxidisation.
9.   Each sample was then dried off in turn, and weighed
10.   The samples were then, in turn, photographed under a microscope for signs of corrosion, including pitting, and discolouration
11.   The corrosion rate was estimated (mg/m^2 hour), and tabulated for each sample
12.   A matellographic investigation of the microscope results was presented

5.   EXPERIMENTAL RESULTS AND CALCULATIONS

Table 1. Experiment results for test samples   *Continued overleaf…*

Copper; Aluminium alone in heater at 40°C for 17 hours

Sample	Copper mass (g)	Cu Area (cm^2)	After test mass (g)	Cu Mass loss (g)	Aluminium mass	Al Area (cm^2)	After test mass (g)	Al Mass loss (g)
1:C18	7.9154	5.7000	7.9081	0.0000073	4.5754	5.510	4.5750	0.0000004
1:E17	8.0956	5.7700	8.0940	0.0000016	4.3748	5.415	4.3748	0.0000000
2:C18	7.9441	5.7380	7.9376	0.0000065	4.6047	5.686	4.6040	0.0000007
2:E17	8.0400	5.7570	8.0390	0.0000010	4.6164	5.700	4.6164	0.0000000

Cu **AND** Al Mass in heater at 40°C for 17 hours

Sample	Copper mass (g)	Cu Area (cm^2)	After test mass (g)	Cu Mass loss (g)	Aluminium mass (g)	Al Area (cm^2)	After test mass (g)	Al Mass loss (g)
1: C18	3.9755	8.4830	3.9755	0.0000000	0.8459	3.74	0.8373	0.0000086
1: E17	4.2389	9.0250	4.2389	0.0000000	1.0783	4.37	1.0783	0.0000000
2: C18	2.5306	5.7760	2.5306	0.0000000	0.8960	3.96	0.8860	0.0000100
2: E17	2.7801	6.1370	2.7801	0.0000000	0.7680	3.08	0.7680	0.0000000

The corrosion rate was determined from (ASTM G1, 1994):

Corrosion Rate = (K x W)/ (A x T x D)

Where:
K Constant (1x10^4 x D for g/m^2. per hour)
T Time of exposure in hours
A Area in cm^2
W Mass loss in grams, and
D Density in g/cm^3   (8.94 for Cu; 2.78 for Al)

Results:

Table 2. Calculated results for corrosion rates of aluminium and copper

Corrosion rate ($g/m^2.hr$)	Cu; Al seperately		Cu + Al together
Sample	Cu	Al	Al
1:C18	0.00084	5.14259E-05	0.000499
1:E17	0.00018	0	0.000000
2:C18	0.00074	8.94227E-05	0.000548
2:E17	0.00011	0	0.000000

6.   METALLOGRAPHIC INVESTIGATION

The samples were each examined under a microscope for different signs of corrosion. A the sample was first cleaned of dust, then placed onto a piece of plasticine, which in turn was placed on a glass plate. The metal was pressed into a flat position. The metal was then scanned for corrosion features at magnification factors of 5, 10, 20, and 50 depending on the size of pitting. Photographs were taken electronically at each respective magnification factor, and the average pitting diameter measured. Figure 1. illustrates the copper samples analysis, where no pitting was observed. Table 2. overleaf illustrates the microscopical analysis for each of the aluminium samples. Pitting corrosion, of varying degrees, was observed on all of the samples.
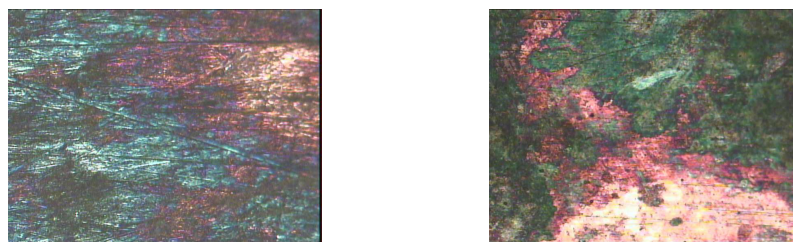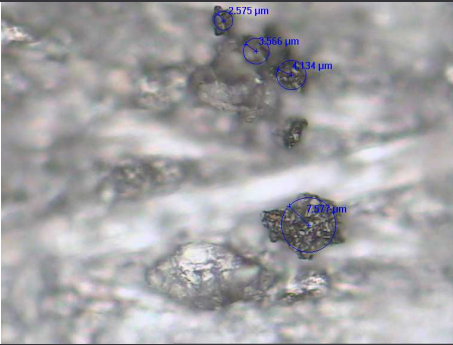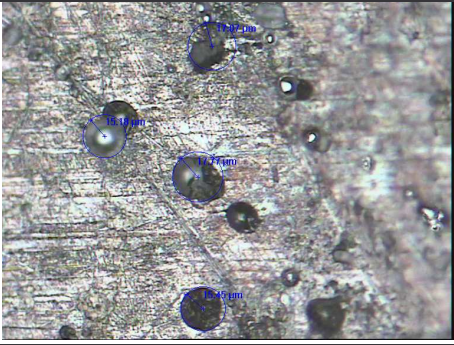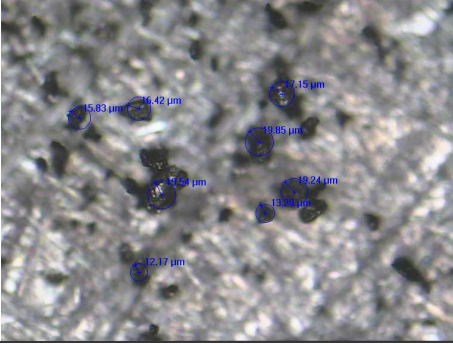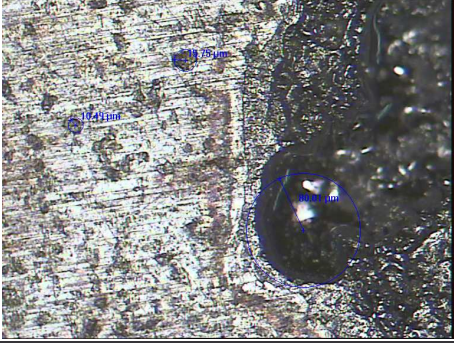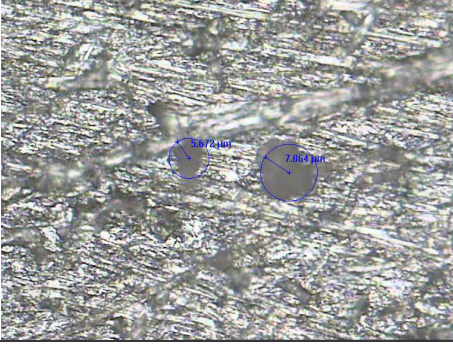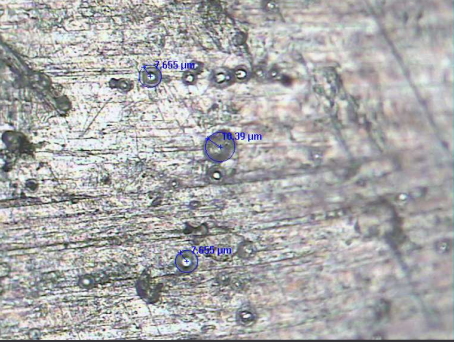

Figure 1. Microscopical examination of a copper sample tested alone (left) and a sample tested with aluminium (right)

Table 3. Microscopical examination of the aluminium samples

Test 1: Aluminium separate	Test 2: Aluminium with Copper
Sample 1: C18, Magnification factor X10. Pitting across surface between 20 – 30μm	Sample 1: C18, Magnification factor X20. Pitting observed across the surface between 2.5-25.5μm

Sample 1: E17, Magnification factor X50. Pitting observed across surface between 2.5-7.5µm	Sample 1: E17, Magnification factor X20. Pitting observed at points on surface between 2.5-17.5µm
Sample 2: C18, Magnification factor X10. Pitting observed across surface between 12-20µm	Sample 2: C18, Magnification factor X10. Pitting observed across the surface between 10-80µm
Sample 2: E17, Magnification factor X50. Pitting observed across surface between 2.5-8µm	Sample 2: E17, Magnification factor X20. Pitting observed at points on surface between 2.5-10.5µm

7.   SUMMARY AND DISCUSSION

There was no pitting observed on any of the copper samples. There was however varying degrees of discolouration, with greatest observed on those samples that were immersed alongside the aluminium samples in common PCM containers. The discolouration highlighted a form of chemical corrosion from chloride ion concentration at the surface. Localised pitting corrosion was observed on all aluminium samples. The greatest pitting was observed on those samples immersed in the C18 PCM, of which the most severe cases occurred when coupled with copper samples where galvanic corrosion occurred. The least pitting was observed on the E17 PCM samples.

8.   PREVENTATIVE MEASURES

Ure (2003) used tin plating of copper fins for experimental analysis of heat pipe heat exchangers with sodium chloride based salt hydrate PCMs heat sinks. Tin in that instance was most appropriate because it has the least potential difference between all other anodic metals. With heat pipe heat exchangers, the casing is aluminium, and the pipes are copper onto which aluminium fins are expanded, thereby plating the entire plate with aluminium. However, minor cracks or deformations may form, and, In such case, the copper is Cathodic, the aluminium is anodic, the PCM acting as the electrolyte.

The Corrosion and Protection Centre (CPC, 2002) report that Magnesium and magnesium allows, zinc, commercially pure aluminium, then cadmium, A sacrificial anodic metal such as zinc or ideally Cadmium could be used to protect an enclosure consisting of both copper and aluminium. Ideally therefore, Magnesium and alloys would serve best as sacrificial anodes which could be placed into the electrolyte (into the heat exchanger); but the potential difference is up to 0.7V (*cf just 0.1V for copper with Tin plating for example*) (galvanic series). Cadmium is the most suitable at just –0.2V potential difference between materials. Zinc is most practical.

Where a sacrificial anode such as zinc is used to reverse the corrosive effect of the aluminum (now the cathode with respect to the zinc), then its area should be larger than the aluminum. In the heat exchanger layout, the section housing the PCM should be construct, in so far as practicable, from zinc or magnesium: that is, the top and bottom covers to the chamber, and all walls, including the air side heat exchanger. Furthermore, due to the poor congruency characteristics of the PCM, the depth should not be greater than 50mm or the salts will become incongruent, and unusable (Ure, 2003). The shelves required should therefore be constructed from zinc. If still insufficient area is available for anodic corrosion of the zinc, then further 'sacrificial perforated zinc plates' could be used, immersed in the PCM (electrolyte) within the top (and base if necessary) chambers. Figure 1, illustrates the concept.
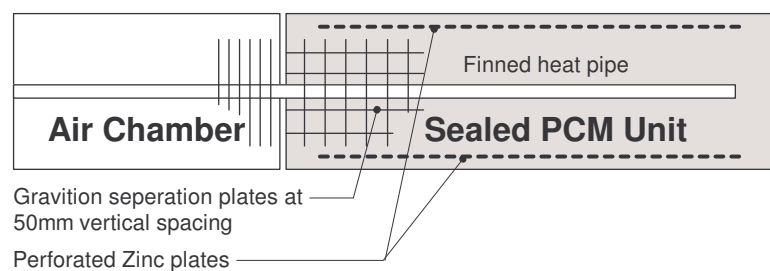

Figure 1. Corrosion prevention measures for low energy heat exchanger

9.   CONCLUSIONS

The samples copper demonstrated the greatest mass loss, varying on average between 0.8 and 0.145 g/m^2.hr for ClimSec C18 and EPS E17 respectively. In contrast, similar area samples of aluminium showed pitting corrosion at a mass loss of, on average, $7x10^{-5} g/m^2$.hr but just for the ClimSel C18 individual samples. The corrosion rate of the E17 samples was too low to be measured, nevertheless, similar localised pitting was observed from the

metallographic examination. Pitting occurred on all samples, and ranged from between 2.5 and 8μm for E17 individual samples; increasing up to 30μm for the C18 individual samples.

Galvanic corrosion was greatest in the second 'mixed sample' tests, where mass loss was recorded again, only for C18 PCM solution with aluminium samples (anodic corrosion). Furthermore, no mass loss occurred with all copper samples as expected (cathodic corrosion). The corrosion rate in the C18 immersed aluminium samples increased by, on average, a factor of eight, as result of the area imbalance (average copper area of 7.13cm^2, average aluminium area 3.85cm^2). Pitting diameters increased dramatically for all the aluminium samples in the galvanic corrosion tests, ranging from 2.5 to 17.58μm across the surface for E17 samples and up to 25μm for the C18 samples. Substantially increased localised deep pitting also occurred on these samples, ranging from 650 to 800+ μm.

A conventional aluminium fin expanded copper heat pipe heat exchanger will offer greatest resistance to galvanic corrosion with minor modifications. The modifications involve plating the housing chamber and PCM gravity separation plates with zinc. If there insufficient zinc area (les than the aluminium area) then further perforated plates may be inserted into PCM chamber above and below the fin matrix to offer the required sacrificial corrosive area. Finally, a suggested design for such a heat exchanger is proposed, for use with hydrated salt phase change materials.

REFERENCES

1. ASTM (1994) 'Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, Annual book of ASTM standards, section 3, metals test methods and analtical procedures, Vol 3.02, G1 - 90 (1994), American Society for Testing and Materials (ASTM), West Conshohocken, PA, US
2. Cabeza, L.F, Roca, J. Illa, J., Badia, F., Mehling, H., Hiebler, S., and Ziegler, F. (2001b) Immersion corrosion tests on metal-salt hydrate pairs used for latent heat storage in the 32 to 36 C temperature range, Materials and Corrosion, Vol. 52, 140 - 146.
3. Cabeza, L.F, Roca, J. Illa, J., Badia, F., Mehling, H., Hiebler, S., and Ziegler, F. (2001c) 'Middle term immersion corrosion tests on metal-salt hydrate pairs used for latent heat storage in the 32 to 36 C temperature range', Materials and Corrosion, Vol. 52 , 748 - 754.
4. Cabeza, L.F, Roca, J. Illa, J., Badia, F., Mehling, H., Hiebler, S., Ziegler, F. (2001a) 'Corrosion experiments on salt hydrates used as phase change materials in cold storage', International Enegy Agency (IEA) ECES IA Annex 17 Kick-o. Workshop, Lleida, ES
5. Cabeza, L.F., Roca, J., Nogues, M., and Mehling, H. (2002) 'Immersion corrosion tests on metal-salt hydrate pairs for latent heat storage in the 48 to 58°C temperature range', Materials and Corrosion, Vol. 53, (2002), pp. 902-907
6. Climator (2003) Product information sheet visited online at http://www.climator.com/products/pouches.html on 21.10.03
7. CPC (2002) Localized Corrosion, Module 0 course notes, Corrosion and Protection Centre (CPC), University of Manchester Institute of Science and Technology (UMIST), Manchester, UK
8. Farrell, A.J. (2003) 'Phase Change Material performance in a novel Low Energy Cooling Heating And Daylight system (LECVHAD) PART I: The melting phase', MATRIB 2002,

Croatian Society for Materials and Tribology & Dublin Institute of Technology, Vela Luka, Island Korcula, Croatia, June 2002, IE

9. Farrell, A.J. and Clancy, E. (2002a) 'Innovative hybrid ventilation cooling system for deep plan buildings in maritime climates', *World Renewable Energy Congress VII, [WREN], Cologne, Germany, 29June-5July 2002,* WREN, D

10. Farrell, A.J., Clancy, E., Byrne, D. (2002b) 'Phase Change Material Use In Low Energy Climate Control Systems', 1st International Conference On Materials And Tribology, Dublin September, 2002, IE

11. Porisini, F.C. (1988) 'Salt hydrates used for latent heat storage: corrosion of metals and reliability of thermal performance', Solar Energy, Vol. 41, 2, pp. 193-197

12. Schweitzer, P (1983) Corrosion and Protection Handbook¸ Marcel Dekker imprint

13. Shreir. L.L (1976) Corrosion, Vol.1, Metal/environment reactions, Newnes-Butterworths, London

14. Ulfvengren, R. (2003) Personal communication with Rolf Ulfvengren of Climator regarding characteristics of ClimSel C18, and visit to Climator homepage at www.climator.com on 21.10.03

15. Ure, Z. (2003) Personal communication with Zafer Ure regarding characteristics of 'PlusICE E17' PCM solution (21.10.03); and visit to EPS homepage at http://www.epsltd.co.uk/frame.html?plusicemain.htm on 21.10.03.

16. Zalba, B., Marin, J.M., Cabeza, L.F., and Mehling, H. (2003) 'Review on thermal energy storage with phase change: materials, heat transfer analysis and applications', Applied Thermal Engineering, Vol. 23, (2003), pp. 251-283