DURABILITY OF SOLAR SELECTIVE ABSORBERS UNDER CONDENSATION TEST

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Abstract

The paper focuses on the performance and durability of modern aluminium based solar thermal absorbers. The solar absorber is strongly influencing the collector's efficiency. Although there are several studies concerning the durability of solar selective absorbers, the focus was mainly on the optical changes. However, the external factors from the environment can lead to chemical modifications and diffusion problems in the coatings, which are not well documented. High humidity and condensation favours electrochemical corrosion, hydratization reactions and, thus optical degradation. A constant condensation test was performed to evaluate the effect of moisture on two solar absorber coatings performance. The objective was to better understand the degradation mechanism. Optical and microstructure modifications after different time intervals were assessed using UV-Vis-IR spectroscopy and photo-electron spectroscopy (XPS). Following the new ISO 22975-3 standard, the samples were first tempered. The thermal treatment can slightly increase or decrease the optical performance due to some possible physical modifications in the layers. The main degradation mechanism identified is the aluminium diffusion to the top layer and then corrosion in high humidity. Although there is a decrease of their optical properties, both absorbers selected for this study can be qualified according to the new ISO 22975-3:2014 standard with respect to their resistance to condensed water. More investigations are required to increase the fundamental knowledge about solar absorber degradation.

1 Introduction

Implementing large scale renewables systems is a sustainable way to obtain energy supply security and climate protection. One of the main priorities of European Union (EU) is to become world number one in renewable energy systems [1]. Solar thermal is a key energy supply with a large untapped potential. Heating and cooling is responsible for nearly half of Europe's energy demand and a significant percentage could be covered

by solar thermal. However, solar heating and cooling (SHC) sector has been for a long time neglected at EU level. The Renewable Energy Sources Directive [2], the Energy Performance of Buildings Directive [3] and other regulatory policies [4] try to integrate SHC into the European energy strategy. Some ambitious targets like $1m^2$ of collector area for every European can only be reached by implementing public policies, creating innovative collectors (e.g. integrated into buildings), and by quality assurance and developing (new) standards for all the solar thermal products. Although some pre-standards and standards are already operational and generally accepted, work is still necessary in order to keep track with recent technological progress (e.g. new materials, new technologies, etc.). Standardization methods are necessary to assess the collector's efficiency, but also durability of solar thermal systems and materials [5].

The solar collector is the key component) of a solar thermal system. High conversion efficiencies are obtained by using solar selective absorbers. However, the long term behaviour and the expected service life time must be also considered when selecting materials [6]. For selective absorbers, beside of oxygen, moisture and condensed water may lead to different degradation reactions, chemical/layers modifications and/or diffusion problems in the coating. Usually, selective absorbers are based on metal/metal oxides (cermet) [7] or metal nitrides which may undergo hydratization reactions increasing the thermal emittance of the coating [8]. Also, electrochemical corrosion and washing of the surface layer can occur in high humidity and condensation. All these degradation mechanism can have a strong effect on the optical properties [9]. The ageing phenomena of absorber surfaces in high humidity and condensation have been investigated in relatively few studies. Some coatings cannot be qualified with respect to their resistance to condensed water, although the temperature test is passed. The absorber surface durability was former assessed using the qualification procedure developed by the IEA Task X group. This recommended procedure was replaced last year by the new ISO 22975-3:2014 standard.

The paper presents first results from the SCIEX project *ColourAge - Accelerated ageing test procedures for coloured selective absorbers of solar collectors,* developed at SPF Institute for Solar Technology, Switzerland. The project focuses on the performance and durability prediction of aluminium based solar thermal absorbers. Comparative water condensation tests are developed for standard multilayers absorber coatings and for novel coloured absorbers made by Transilvania University of Brasov [10].

The effect of tempering and humidity in terms of optical changes is discussed for two types of solar selective absorbers. The modifications from the previous test procedure compared to the new standard for assessing the absorber durability are highlighted. The degradation mechanism is also discussed for one type of absorber.

2   Experimental part

Two types of modern solar selective absorbers obtained by Physcial Vapor Deposition were tested in high humidity and condensation at *40°C, 95% RH*. As can be seen from Table 1, the two absorbers are nearly equivalent concerning their optical properties. A climatic chamber (Horstmann HS 220 K 45, volume 0.22 m3) with a cooled sample holder for controlling the sample temperature (Lauda RK8 KP) was used. The samples (5x5 cm) were exposed to high humidity and condensation (HHC): a) absorber A: shorter testing time (max 384 h), b) absorber B: long term testing time (max 600 h). Optical measurements (Bruker IFS66) were performed for different testing time intervals and the following parameters were calculated:

- *solar absorptance* (α_s) which represents the fraction of solar radiation energy absorbed by the absorber surface;
- *thermal emittance* ($\varepsilon_{t,\,100}$) which represents the ratio between the energy (per unit area) radiated by the absorber surface at 100°C and the corresponding energy radiated by a perfect black body at the same temperature;
- *performance criterion* function which shows the changes in performance of an absorber surface in terms of solar absorptance and thermal emittance (Eq. 1), where $\Delta\alpha_s$ is the change in the solar absorptance ($\alpha_{s,t}$ is the solar absorptance at the actual testing time and $\alpha_{s,i}$ is the initial solar absorptance), and $\Delta\varepsilon_{t,100}$ is the change in the thermal emittance (with ε_t - the thermal emittance at the testing time t and ε_i is initial thermal emittance. For simplification, the symbol ε will be used for the thermal emittance further on.)

$$PC = -\Delta\alpha_s + 0{,}50\ \Delta\varepsilon_{t,100} \leq 0{,}05 \qquad \textit{Eq. 1}$$

$$\text{where: } \Delta\alpha_s = \alpha_{s,t} - \alpha_{s,i}$$

$$\Delta\varepsilon_{t,100} = \varepsilon_t - \varepsilon_i$$

Elemental composition modifications after ageing were studied for the absorber A using photo-electron spectroscopy (XPS). The XPS measurements were performed with a VG ESCALAB 210 spectrometer using monochromatized Al Kα radiation (1486.6 eV) with an energy resolution better than 0.8 eV for 20 eV pass energy. Normal electron escape angle and a step size of 0.05 eV were used. The spectra were not charge corrected. Fitting of the core level lines was performed using Doniach-Sunjic (asymmetrical Lorentzian) functions [11], with a background subtraction [12], using UNIFIT for

Windows (Version 2013) software [13]. A convolution of an asymmetry function, Lorentzian and Gaussian line shapes were used to fit the individual peaks. After this, the intensities were estimated by calculating the integral of each peak; the atomic concentrations were then derived using Scofield sensitivity factors [14].

Table 1 Solar selective absorbers tested for determining their resistance to condensed water

	Absorber A	Absorber B	Samples for condensation
Substrate	Aluminium	Aluminium	
Solar absorptance	0.95	0.95	
Thermal emittance	0.05	0.04	
Maximum width	1250 mm	1250 mm	
Thickness	0.2÷0.5 mm	0.20÷0.75 mm	
Warranty	10 years	10 years	

3   Results and discussion

3.1   Sample conditioning

The preparation of test specimens is slightly different compared to the previous recommended procedure from Task X. According to the new ISO 22975-3:2014 standard procedure, a minimum of 18 test samples are required. Previously, a minimum of 21 samples were required. The mean solar absorptance and mean thermal emittance must be determined for three test samples. Then, the possible maximum absorber temperature is determined for the case of a collector with anti-reflection coating. All 18 samples must be tempered at this temperature for at least 5 h and then, the optical properties are measured. This procedure was introduced to better distinguish between real long term degradation and initial tempering effects. In order to be qualified for testing, the standard deviation for the solar absorptance should be less than 0.01, while for the thermal emittance should be less than 0.04. Moreover, three samples are tested to check the adhesion. If these conditions are fulfilled, then the samples are qualified for testing.

Following these steps, the samples were tempered at 211°C (absorber A) and 213°C (absorber B), respectively. The variation of the solar absorptance (α_s) and thermal emittance (ε) before and after tempering is presented in Fig. 1. Tempering has a different effect on the two absorbers. In case of absorber A, the average solar

absorptance value is decreasing from 0.955 (un-aged) to 0.945 (tempered), while the average emittance value is increasing from 0.056 (un-aged) to 0.061 (tempered). A different behaviour is registered for absorber B: the average α_s is increasing from 0.959 (un-aged) to 0.960 (tempered), while epsilon is decreasing from 0.054 to 0.049. Thus, tempering can slightly increase or decrease the optical performance due to some physical modifications in the layers, water evaporation, re-arrangements, coalescence and possible surface morphology modification. In the un-tempered stage the optical properties of the two absorbers are nearly identical, with a slightly higher performance of absorber A. However, the changes in optical properties are leading to a performance gain for absorber B, but to a performance loss for absorber A. After tempering, the performance of absorber B is more than two per cent better than absorber A (according to the performance criterion PC defined above).
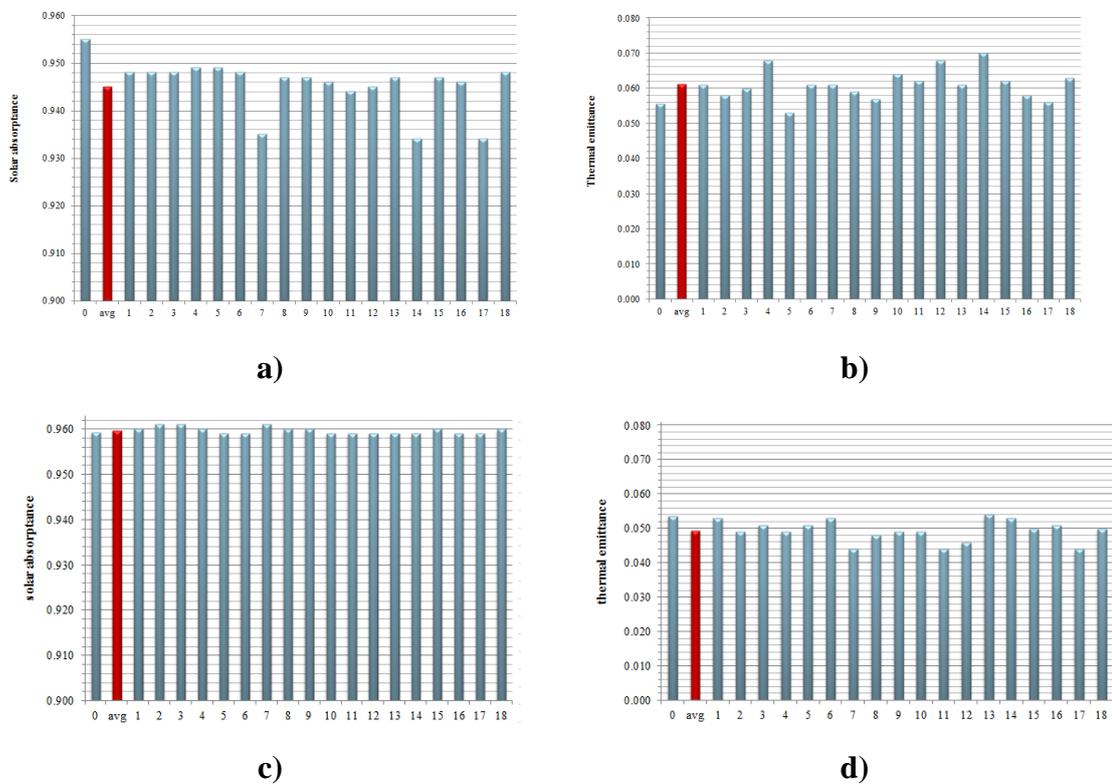
Fig. 1 Solar absorptance and thermal emittance for absorber A (a, b) and for absorber B (c, d) before and after tempering (0 represents the average value calculated for 3 samples from the un-aged absorber and 1-18 are the values for the tempered samples, while avg represents the average value for all 18 tempered samples

3.2 Absorbers surface resistance to condensed water – optical modifications

A constant condensation test was performed to evaluate the effect of moisture on the coatings performance. At least two different constant condensation test should be

performed for two absorber temperatures (40°C and 30°C or 40°C and 60°C), as specified in the ISO 22975-3:2014 standard. However, if PC≤0.015 after 600h of testing at T_1=40°C, and the adhesion requirements are met, the absorber surface can be qualified with respect to its resistance to condensed water only by performing a test at 40°C.

Even though both absorbers selected can be qualified with respect to their resistance to condensed water, the objective was to understand better the degradation mechanism. A constant condensation test was performed at 40°C. Shorter testing time intervals are presented in this paper for absorber A for which the change in the optical properties was more accentuated than in the case of absorber B. In the first hours of condensation, a drop of the solar absorptance is registered for absorber A (Fig. 2, a) and then the values are becoming rather constant. The modification of the absorption properties can be the result of surface morphology modification and/or due to changes in layer structure/composition. The thermal emittance is slowly increasing (Fig. 2, b). An opposite behaviour is registered for the absorber B (Fig. 2).

a)   b)
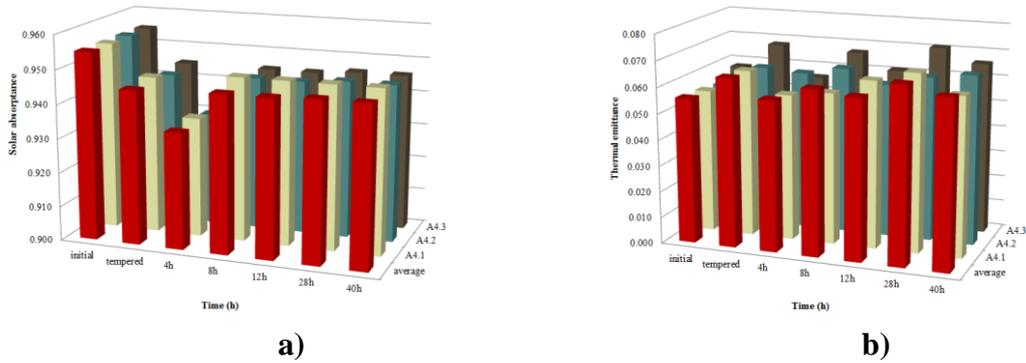
*Fig. 2 Solar absorptance (a) and thermal emittance (b) for the un-aged and aged **absorber A**, where average represents the average value for the three tested samples*

a)   b)
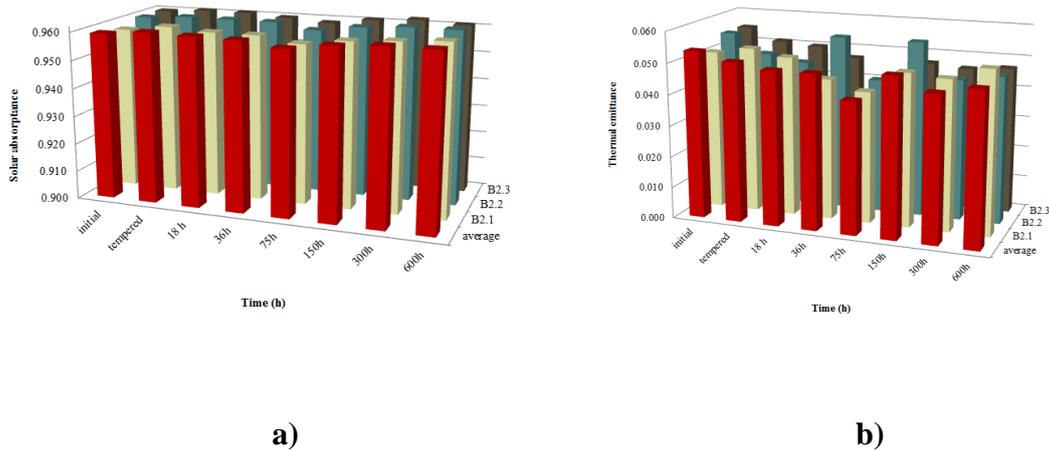
*Fig. 3 Solar absorptance (a) and thermal emittance (b) for the un-aged and aged **absorber B** where average represents the average value for the three tested samples*

Both solar absorbers present low values of the performance criterion (i.e. are qualified), much lower than the maximum value (0.05) (Fig. 4, a and b).

a)   b)
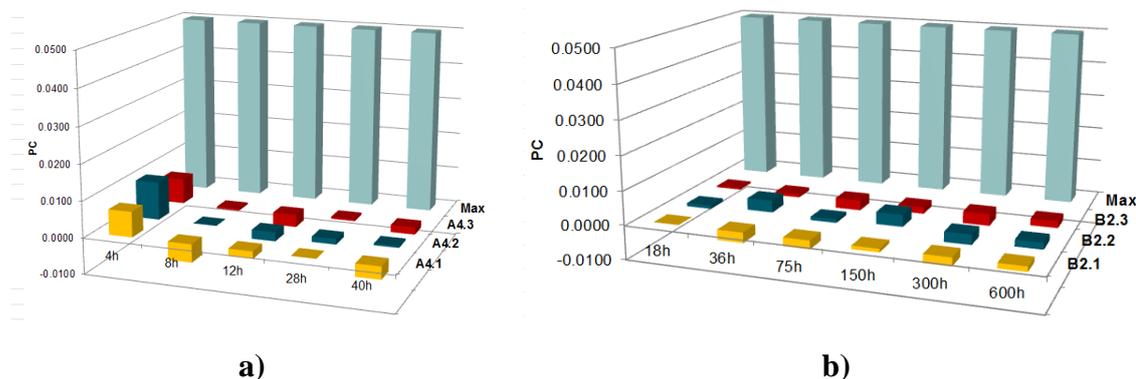
*Fig. 4 Performance criterion corresponding to the **absorber A** (a) and **absorber B** (b) after 40 h of testing, and 600 h of testing, respectively*

The optical degradation must be correlated with the morphology changes, layers structure and chemical modification. Photo-electron spectroscopy was performed for absorber A (after 16 days of ageing). However, more investigations are needed to better understand the degradation process.

3.3   Absorbers surface resistance to condensed water -chemical modifications

X-ray photoelectron spectroscopy (XPS) measurements indicate one degradation mechanism in high humidity and condensation for solar selective coatings based on aluminium: diffusion of aluminium. XPS measurements were performed for the absorber A as received and after 10 and 35 minutes of Ar sputtering at 2.5 keV M (Fig. 5). The results show that the top layer contains not only silicon (Si2p) and oxygen (O1s), but also aluminium (Al2p) and carbon (C1s) contamination. Kotilainen et al have performed ageing studies of solar selective coatings at high temperature [15] and they have also reported the diffusion of substrate atoms into the coating or through the coating to the surface for the aged absorber.

Aluminium can form two different compounds: amorphous Al_2O_3 layer and a hydroxide layer with thickness depending on the environmental temperature and humidity. The difference between different Al-O phases can be obtained from the O1s and the Al2p-peak of the XPS-spectra. The Al-oxide peak from the Fig. 5 spectra indicates both the presence of Al_2O_3 and Al-hydroxide. The O1s-peak shows differences between the two forms: Al_2O_3 has the O1s-peak maximum at the lowest binding energy; Al-hydroxide has a small shifting of the O1s-peak to higher binding energies as well as a broadening of the signal[16]. According to literature and to the binding energies, the top layer consists of hydroxide phases (0 min) as well as oxide (18 min).

The atomic concentrations calculated by XPS are presented in Table 2.

Table 2 Atomic concentration of the sample calculated by XPS as received and after 10 and 35 minutes of Ar sputtering at 2.5 keV

	Si	O	Al	C
As received	29.3	56.9	2.4	11.4
10 min	32.9	58.4	2.7	6.1
35 min	35.1	58.6	2.7	3.6
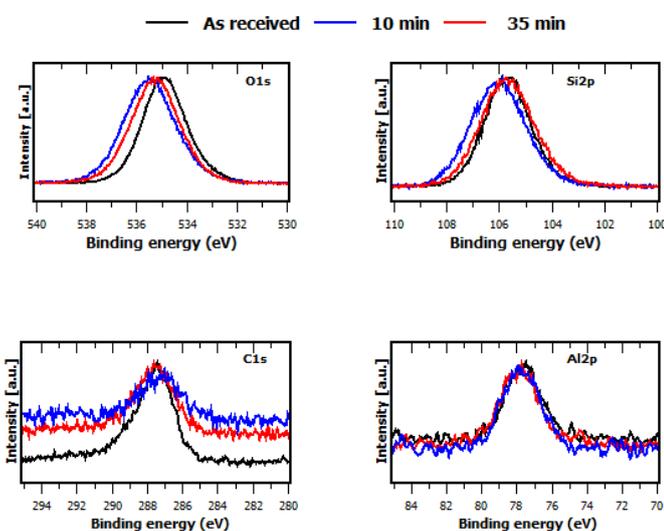
Fig. 5 XPS core level spectra of O1s, Si2p, C1s and Al2p measured as received and after 10 and 35 minutes Ar sputtering at 2.5 keV

4   Conclusions

The effect of tempering on the optical properties of solar selective absorbers was studied. Possible degradation mechanisms in high humidity and condensation humidity are also presented. For assessing the absorber surface durability to condensation, the ISO 22975-3:2014 standard was used. Published in July 2014, the standard is based on the recommended procedure developed in IEA Task X. The main modification in the new standard is that the test samples must be tempered before ageing, at least 5 hours at the maximum possible absorber temperature. This temperature is determined for the case of a collector with anti-reflection coating, based on the average solar absorption

and thermal emittance values calculated for three test specimens. The tempering process can slightly increase or decrease the optical performance due to some possible physical modifications in the layers, water evaporation, re-arrangements, coalescence and surface morphology modification.

Both absorbers selected for this study can be qualified with respect to their resistance to condensed water. However, the objective was to understand the initial absorber degradation in high humidity and condensation. The modifications of the optical performance are due to surface morphology modification and due to changes in layer structure/composition. The SEM and XPS measurements revealed that aluminium is diffusing to the top layer, and then it is forming more or less stable Al-O forms. The layers are modified due to water infiltration, hydratization and diffusion. More investigations will be performed.

5 Acknowledgement

6   References

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