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Solar Energy Materials & Solar Cells

Solar Energy Materials & Solar Cells I (IIII) III-III

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# Thermal stability and moisture resistance of C/Al<sub>2</sub>O<sub>3</sub>/Al solar absorber surfaces

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Received 20 May 2003; received in revised form 20 August 2003; accepted 19 December 2003

#### Abstract

Mechanically manufactured C/Al<sub>2</sub>O<sub>3</sub>/Al solar absorber surfaces were exposed to thermal stability and moisture resistance tests following the IEA Solar Heating and Cooling Programme recommendations (draft ISO/DIS 12592). The main degradation mechanism is found to be hydration of aluminium oxide to pseudoboehmite and boehmite. We estimated the absorber service lifetime (with an optical performance more than 95% of its initial) based on two literature references, where time of wetness frequency distribution of a solar collector microclimate was measured. The estimated average service lifetime in normal use was 20 or 25 years, depending significantly on the time of wetness frequency distribution of the surface.  $\bigcirc$  2004 Elsevier B.V. All rights reserved.

Keywords: C/Al<sub>2</sub>O<sub>3</sub>/Al solar absorber; Mechanical manufacturing; Accelerated aging tests; Hydration

#### 1. Introduction

Accelerated aging tests of solar absorber surfaces are used to estimate the service lifetime of a solar collector [1–6]. Minimum service lifetime of 25 years is a commonly used target when designing new absorbers. The maximum service lifetime of an absorber coating is reached if the annual solar fraction of a domestic hot-water (DHW) system is decreased by 5% due to deterioration of its optical properties caused by degradation [6]. The absorber can still be used after the maximum service lifetime has been reached, if the owner accepts the lower performance. Tests are

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typically conducted under three different conditions: high temperatures and low humidity, service temperatures under condensation conditions and service temperatures and high-humidity air containing sulphur dioxide [2–6]. The IEA Solar Heating and Cooling Programme (IEA SHC) Working Group "Materials in Solar Thermal Collectors" has proposed a procedure based on these tests as a standard to the ISO TC 180 'Solar Energy' [4].

We designed and conducted a series of accelerated aging tests in order to determine the service lifetime of mechanically manufactured selective  $C/Al_2O_3/Al$  absorber samples. The principles and methods of the surface manufacturing are described in [7]. The microstructural composition of the surface consists of a graphite–alumina groove matrix on Al substrate. A detailed microstructural analysis is communicated in [8].

In this paper, the methods and results of the high-temperature and combined elevated temperature and high-humidity/condensation tests are reported. These tests were mainly conducted according to the IEA SHC recommendations [1–6] with some additional tests. Standard SO<sub>2</sub> tests were not conducted due to absence of equipment needed, but they have been replaced with a more severe test, where absorber samples are subjected to simulated acid rain containing sulphuric acid at temperature range of 60–100°C and duration up to 14 days. These results will be published separately after concluding the tests.

#### 2. Instrumentation and measurement equipment

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A high-temperature air-circulating oven was utilized for thermal stability testing. Temperature accuracy and uniformity inside the oven is within  $\pm 1^{\circ}$ C. The oven meets the IEA SHC testing equipment requirements [5] for assessing the thermal stability of an absorber surface, except for the cooling rate requirement. Therefore, the test panels were removed from the oven immediately after the specified testing time was reached, as recommended in [5].

A climate chamber (model Arctest ARC 400) with a 3541 inner volume and a temperature range between  $-40^{\circ}$ C and  $+120^{\circ}$ C was used for moisture testing. The climate chamber is able to maintain temperature within  $\pm 1^{\circ}$ C and relative humidity within  $\pm 2-3\%$ , after stabilized conditions have been reached. The absolute accuracy of temperature and humidity is within  $\pm 1\%$  at the measurement point. Uniformity of the temperature depends on the operation mode, being in the range of  $\pm 1^{\circ}$ C during these tests. Sample holders, similar to the ones used by Carlsson et al. [2] were used to cool the samples and to keep them electronically insulated. The climate chamber meets the IEA SHC testing equipment requirements for assessing the resistance of the absorber surface to moisture [5].

Total hemispherical AM 1.5 solar absorptance,  $\alpha$ , and total hemispherical thermal emittance (at 100°C),  $\varepsilon$ , of the samples were measured before and after each test at room temperature.  $\alpha$  was determined between 0.39 and 1.1 µm with an LI-COR LI-1800 type spectroradiometer and a BaSO<sub>4</sub>-coated integrating sphere.  $\varepsilon$  was determined between 2.5 and 20 µm with a MIDAC Prospect FTIR-spectrometer

with a semi-integrating device. More details about the measuring procedures are published in [7]. Reference measurements for some samples were conducted at the Ångström laboratory of the Uppsala University. The reference equipment consists of a Beckman UV 5240 spectrophotometer with a  $BaSO_4$ -coated integrating sphere for UV–Vis–NIR and a Bomem Michelson 110 FTIR spectrometer with a gold-coated integrating sphere for IR.

According to Brunold et al. [4], the optical homogeneity of the samples is of most importance for reliable test results. To be qualified for testing, the standard deviation  $\sigma_{\alpha}$  for  $\alpha$  of new samples must be less than 0.01 and the standard deviation  $\sigma_{\varepsilon}$  for  $\varepsilon$  must be less than 0.04. The samples used in these tests comply with these limits.

## 3. Experimental procedure

For estimating the acceptable service life of an absorber coating, the IEA SHC Task X [2] has defined a performance criterion function (PC):

$$PC = -\Delta\alpha + 0.25\Delta\varepsilon < 0.05. \tag{1}$$

When the value of the PC function has been increased to 0.05, the solar fraction of a DHW system has been reduced by around 5% in relative sense for a low-fraction flat-plate collector solar DHW system [5]. The absorber surface should consequently be considered failed, due to degradation in the optical performance.

Several papers [5,6,9] have been published describing the testing procedure for the thermal stability and high-humidity/condensation tests according to the IEA SHC recommendations (draft ISO/DIS 12592). Thermal stability test consists of an initial test at 250°C for 200 h followed with an adhesion test. The sample is qualified without further tests, if the surface adhesion  $\ge 0.15$  MPa and PC < 0.015 after the test (before test adhesion must be  $\ge 0.5$  MPa). Otherwise, additional tests are required at different temperatures.

Moisture tests consist of initial tests at absorber panel temperature of  $40^{\circ}$ C for 80–600 h [5]. Absorber samples are cooled down 5°C below the chamber temperature thus causing continuous condensation on the surfaces. Subsequent tests depend on the initial test results. In order to determine the Arrhenius activation energy related to the degradation, another test at sample temperature of either  $60^{\circ}$ C or  $30^{\circ}$ C is required. The test absorber panel size is  $50 \text{ mm} \times 50 \text{ mm}$  for all tests.

The adhesion of the coating prior and after each test can be assessed by a procedure standardized in ISO 4624 or by a simple tape test. For  $C/Al_2O_3/Al$  absorber surfaces, tape test was applied with an acrylic foam tape. The tape manufacturer claims normal tensile of this tape to be  $110 \text{ N cm}^{-2}$  which exceeds the IEA SHC requirement [5].

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## 4. Results

#### 4.1. Thermal stability

Thermal stability of C/Al<sub>2</sub>O<sub>3</sub>/Al absorber surfaces was tested according to the IEA SHC recommendations (draft ISO/DIS 12592) [5]. Three unaged samples were exposed to 250°C for 200 h. The mean  $\alpha$  increased from 0.88 to 0.89 and the mean  $\epsilon$  increased from 0.27 to 0.28. Mean spectral reflectance between 0.39–1.1 and 2.5–20 µm before and after aging is shown in Fig. 1 (see Section 4.4 'Source of errors' for significance of the missing wavelength range). The peak between 8 and 10 µm is probably caused by using a specularly reflecting mirror as a reference instead of a diffusely reflecting reference material. Reasons for this procedure are related to the geometry of the semi-integrating device used in the FTIR spectrometer and are thoroughly communicated by Halme in [10]. The PC = -0.004, which is well within the criterion (PC ≤ 0.015). Therefore, no further thermal stability tests were necessary. Changes of the spectral reflectance covering the whole UV–Vis–IR spectrum of a sample subjected to 6 h at 400°C are shown in Fig. 2 (measured at Uppsala University). For this sample PC = -0.005.

In order to test the thermal stability of an aged surface, a solar collector was disassembled after 4 years of natural exposure at a test site (in Espoo, Finland,  $60^{\circ}11'$  N,  $24^{\circ}49'$  E) and three surface samples were tested at  $250^{\circ}$ C for 200 h. The mean  $\alpha$  did not change:  $\alpha_{0h} = \alpha_{250h} = 0.89$ ,  $\Delta \alpha = 0.00$ , the mean  $\varepsilon$  increased from  $\varepsilon_{0h} = 0.30$  to  $\varepsilon_{250h} = 0.35$ ,  $\Delta \varepsilon = 0.05$  (Fig. 1). PC = 0.013, which is within the criterion limit as well. It must be noted that these samples represent earlier stage of production [7] and therefore  $\varepsilon$  of the latest samples (being originally lower) does not probably rise to the same level after natural and/or accelerated aging. Different manufacturing

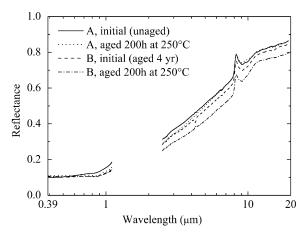


Fig. 1. Changes of the spectral reflectance of a  $C/Al_2O_3/Al$  absorber surface samples due to high-temperature degradation: (A) mean values of three previously unaged samples; and (B) mean values of three samples taken from disassembled collector, which was naturally aged for 4 years at a test site. Wavelength ranges measured include 0.39–1.1 and 2.5–20  $\mu$ m.

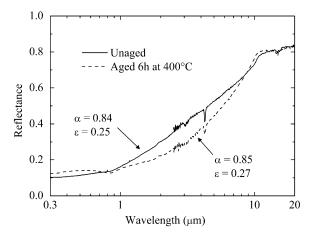


Fig. 2. Changes of the spectral reflectance of a  $C/Al_2O_3/Al$  absorber surface reference sample due to high-temperature degradation, measured at Uppsala University.

procedures can give chemical explanation to the observed difference in behaviour of  $\varepsilon$  upon ageing between the naturally aged and unaged samples: After mechanical grinding, earlier (i.e. naturally aged) samples were subjected to acid bath containing potassium permanganate, cupric nitrate and nitric acid, whereas latest unaged samples were only mechanically grinded (see [7] for manufacturing details). It is likely that acids adsorbed onto the surface structure of the earlier (naturally aged) samples evaporate either partially or completely during heating to 250°C thus changing the optical properties of the 4 year aged surfaces more compared to the latest (unaged) samples.

All the samples passed the adhesion tape test before and after the thermal stability test. Both the unaged surfaces and the surfaces aged naturally for 4 years qualified the IEA SHC thermal stability test procedure [5]. A conclusion is that the optical properties of the  $C/Al_2O_3/Al$  absorber surfaces will not deteriorate by the thermal stress alone during (at least) 25 years of normal operation.

#### 4.2. Moisture/condensation resistance

Series of condensing moisture tests were conducted according to the IEA SHC recommendations (draft ISO/DIS 12592) [5]. First tests were conducted for new (= unaged) samples at 40°C sample temperature for 7, 22, 40 and 80 h. The failure time (required to reach PC=0.05) was estimated to be 30 h by interpolating (Table 1). Similar to thermal stability testing, naturally aged reference samples were tested for 40, 47, 56 and 80 h and the failure time was estimated to be 50 h. Three samples were used for each test. Additional moisture tests at 30°C were conducted as recommended in Ref. [5]. The exposure time required to reach PC=0.05 for unaged and naturally aged samples was 400 and 300 h, respectively (Tables 2 and 3).

Fig. 3 shows mean spectral reflectance between 0.39-1.1 and  $2.5-20 \,\mu\text{m}$  of samples before and after aging at  $30^{\circ}$ C. The peak between 8 and 10  $\mu\text{m}$  was communicated in

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Table 1

Changes of absorptance, emittance and PC of samples exposed to condensation at 40°C.

Unaged samples				4 years naturally aged samples				
<i>t</i> (h)	Δα	Δε	PC	<i>t</i> (h)	Δα	$\Delta \epsilon$	PC	
7	0.04	0.00	-0.04	40	0.03	-0.01	-0.01	
22	0.03	0.18	0.02	47	0.02	0.20	0.03	
40	-0.04	0.44	0.16	56	0.00	0.36	0.09	
80	-0.12	0.57	0.26	80	-0.03	0.44	0.14	

Table 2 Changes of absorptance, emittance and PC of samples exposed to condensation at 30°C

Unaged sample				4 years naturally aged samples				
t (h)	Δα	$\Delta \epsilon$	PC	<i>t</i> (h)	Δα	Δε	PC	
125	0.03	0.03	-0.03	300	0.03	0.31	0.05	
300	-0.01	0.05	0.03					
350	-0.03	0.06	0.04					
400	-0.03	0.07	0.05					

Table 3

Calculated activation energies ( $E_T$ ) of samples exposed to condensation at 30°C and 40°C for the time period needed for PC=0.05. Activation energy sources: Carlsson et al. [2] (identical data in Ref. [6]) and Köhl [9].

Unaged samples				4 years naturally aged samples			
t(h)	<i>T</i> (°C)	$E_T  (\mathrm{kJ}  \mathrm{mol}^{-1})$	Source	<i>t</i> (h)	<i>T</i> (°C)	$E_T  (\mathrm{kJ}  \mathrm{mol}^{-1})$	Source
30	40	165	[2,6]	50	40	153	[2,6]
30	40	186	[9]	50	40	173	[9]
400	30	145	[2,6]	300	30	158	[2,6]
400	30	180	[9]	300	30	190	[9]

Section 4.1 'Thermal stability'. Absorption bands in the IR spectrum are discussed a bit further. Adhesion of samples exposed to 40, 56, 300 and 400 h was tested by the tape test, which all samples passed. The  $C/Al_2O_3/Al$  absorber surfaces passed the IEA SHC recommendations for condensation tests [5,6,9].

Prior to the condensing moisture tests, subsequent non-condensing high-humidity tests were conducted starting from 60°C and 60% relative humidity (r.h.) and ending at 80°C and 80% r.h. Either temperature or humidity were increased by 10 units for each test: first phase included 143 h at 60°C and 60% r.h., second phase 50 h at 70°C and 60% r.h., third phase 48 h at 70°C and 70% r.h., fourth phase 24 h at 70°C and 80% r.h. The sample was visually observed between each phase, because  $\varepsilon$  of the sample could not be measured in

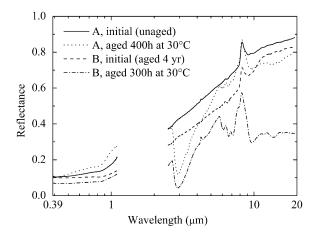


Fig. 3. Changes of the spectral reflectance of  $C/Al_2O_3/Al$  absorber surface samples due to moisture condensation degradation at 30°C: (A) previously unaged sample; and (B) mean values of two samples naturally aged for 4 years.

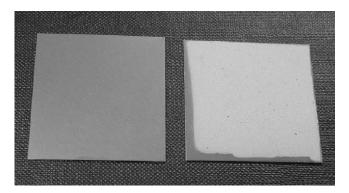


Fig. 4. Photograph of two C/Al<sub>2</sub>O<sub>3</sub>/Al absorber surface samples: unaged (left) and after 24 h at 80°C and 80% relative humidity (right). White layer of boehmite formed due to hydration can be seen on the surface on right. Sample size is  $5 \text{ cm} \times 5 \text{ cm}$  (see Fig. 5 for reflectance data of a new and a hydrated sample).

between without breaking the sample into pieces. A clear visual change on the surface was noted after 24 h at 80°C and 80% r.h. (Fig. 4). Changes in the spectral reflectance were measured at Uppsala University and are shown in Fig. 5.  $\alpha$  decreased from 0.88 to 0.47 and  $\varepsilon$  increased from 0.27 to 0.38.

Carlsson et al. [2,3] have studied degradation of nickel-pigmented anodized aluminium absorber coating. They reported that one main degradation mechanism is hydration of aluminium oxide to pseudoboehmite (AlO  $\cdot$  OH  $\cdot$  XH<sub>2</sub>O, X=0.4–1) and to boehmite ( $\gamma$ -AlO  $\cdot$  OH). They stated that this mechanism requires high humidity or condensed water on the surface of the absorber to be operative. According to Carlsson et al. [3], an indication of hydration is strong absorption bands that appear at 3 µm, between 6 and 7 µm and at around 9 µm, suggesting the formation of

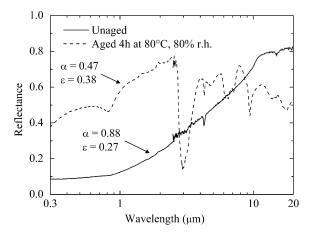


Fig. 5. Changes in the spectral reflectance of a  $C/Al_2O_3/Al$  absorber surface reference sample due to highhumidity degradation at 80°C, 80% relative humidity, measured at Uppsala University.

pseudoboehmite. Such absorption bands at these wavelengths are seen in Fig. 3 (sample B) and Fig. 5, thus suggesting that hydration of aluminium oxide to pseudoboehmite has occurred on the surface of  $C/Al_2O_3/Al$  samples. Absorption band between 6 and 7  $\mu$ m is missing for sample A in Fig. 3 thus suggesting the formation of boehmite and possible other aluminium oxide hydroxides as well [2]. Above about 75°C, the stable oxide form is boehmite [11], which can be seen visually in Fig. 4 and in the absorption bands in Fig. 5. These results indicate that a hydration mechanism similar to the one degrading nickel-pigmented anodized aluminium absorber coating is affecting the mechanically manufactured  $C/Al_2O_3/Al$  absorber surfaces as well.

Non-condensing high-humidity tests for three unaged and three naturally aged samples were conducted inside the climate chamber concurrently with the 30°C moisture tests. After 1000 h at sample temperature of 35°C and chamber humidity of 95% r.h., the mean  $\alpha$  of initially unaged samples had increased from 0.87 to 0.89 and the mean  $\varepsilon$  had increased from 0.24 to 0.26 (PC = -0.015). For naturally aged samples the mean  $\alpha$  had not changed from the initial value of 0.89. The mean  $\varepsilon$  had decreased from 0.29 to 0.28 (PC = -0.01). No sign of hydration was detected either by visual inspection of the samples or in the spectral reflectance (Fig. 6). A malfunction in the equipment after 1300 h severely damaged the samples by high-temperature hydration thus preventing further analyses.

## 4.3. Service lifetime estimates of C/Al<sub>2</sub>O<sub>3</sub>/Al absorber surfaces

We calculated service lifetime estimates based on the assumption that the hydration process is the only significant active degradation process during the service lifetime of the collector. Service lifetime estimates for naturally aged collectors do not include the 4 years of use prior to these tests. Initial values of  $\alpha$  and  $\varepsilon$  were not

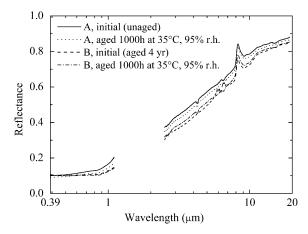


Fig. 6. Changes of the spectral reflectance of a  $C/Al_2O_3/Al$  absorber surface samples due to noncondensation moisture degradation at 35°C, 95% relative humidity: (A) mean values of three previously unaged samples; (B) mean values of three samples naturally aged for 4 years.

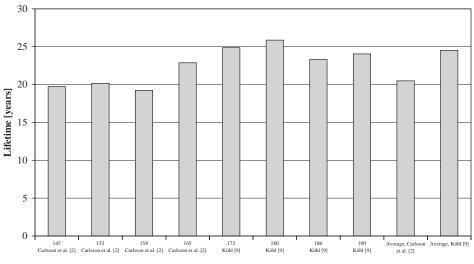
measured for these samples as new and some degradation may have been occurred during the 4 years of natural exposure.

No degradation due to exposure at  $250^{\circ}$ C for 200 h was detected for new samples. Testing of degradation caused by SO<sub>2</sub> has not been done so far. Initial tests of boiling absorber samples with water containing small amounts of H<sub>2</sub>SO<sub>4</sub> showed significantly slower degradation compared to boiling with water without H<sub>2</sub>SO<sub>4</sub> (the full results will be published separately). Carlsson et al. [2] reported electrochemical oxidation of metallic nickel to nickel oxide and nickel sulphate decreasing the absorptance of nickel-pigmented anodized aluminium absorbers. These mechanisms cannot occur for the C/Al<sub>2</sub>O<sub>3</sub>/Al absorbers due to absence of nickel, although similar Al<sub>2</sub>O<sub>3</sub> hydration degradation mechanisms seem to take place for both types of absorber surfaces.

The frequency distribution of the  $C/Al_2O_3/Al$  absorber temperature or collector microclimate humidity was not measured. Collectors with this absorber type delivered to the customers have been supplied with two ventilation holes of about 1 mm in diameter in the side frames of the collector, but ventilation rates inside a collector have not been monitored. Instead, we used reference data from literature sources in order to estimate activation energies and calculate the corresponding acceptable service lifetime for the collector. Reference data included measured time of wetness of collector (nickel-pigmented anodized aluminium absorbers) microclimate during 1 year in: (1) Rapperswil, Switzerland by Carlsson et al. [2] (additional information in [6]) and (2) Zurich, Switzerland by Köhl [9] (four collectors). The temperature dependence of the degradation process was assumed to follow the Arrhenius relationship [2–6,9]:

$$a_n = \exp\left[\frac{E_T}{R}\left(\frac{1}{T_{\text{ref}}} - \frac{1}{T_n}\right)\right],\tag{2}$$

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Activation energy [kJ/mol], load profile source

Fig. 7. Estimated service lifetime of a single-glazed flat-plate solar collector with  $C/Al_2O_3/Al$  absorber surface. Based on calculated Arrhenius activation energies and measured time of wetness load profiles by Carlsson et al. [2] (identical data in Ref. [6]) and Köhl [9] weighted with corresponding acceleration factors.

where  $a_n$  is the Arrhenius acceleration factor,  $T_{ref}$  is the reference absorber temperature (measured in normal use),  $T_n$  is the constant temperature samples are exposed to in the laboratory test,  $E_T$  is the Arrhenius activation energy and R is the ideal gas constant ( $R = 8.314 \,\mathrm{J \, K^{-1} \, mol^{-1}}$ ).

 $E_T$  corresponding to the measured failure time at  $T_n$  of 30°C and 40°C was determined from the nomograms by Brunold et al. [6] (originally published in [2]) and Köhl [9] for each test separately. Subsequently, the Arrhenius acceleration factor  $a_n$  was calculated (Eq. (2)) for  $T_{ref}$  between 0°C and 27°C given in [6,9] by using a temperature step of 1°C. The time of wetness during 1 year load profiles given in [2,9] were normalized to the 25 year service lifetime, weighted with the calculated  $a_n$  (for each  $T_{ref}$ ,  $T_n$  and  $E_T$  separately) and integrated over the  $T_{ref}$  temperature range. The results were compared to the experimental failure times for C/Al<sub>2</sub>O<sub>3</sub>/Al absorber surfaces (i.e. 300 and 400 h at 30°C and 30 and 50 h at 40°C) in order to determine the estimated service lifetime for the absorber surface.

The estimated  $E_T$  based on reference data [2,6] is 145–165 kJ mol<sup>-1</sup> for unaged absorber samples and 153–158 kJ mol<sup>-1</sup> for 4 year aged absorber samples (Table 3). Service lifetime can be estimated to be 19–23 years in both cases (Fig. 7). The estimated  $E_T$  and service lifetime based on data from [9] is 173–190 kJ mol<sup>-1</sup> and 23–26 years, respectively. The average service lifetime estimate based on [2,6] and on [9] is 20 and 25 years, respectively (Fig. 7). The main cause in the variation in service lifetime estimates is the divergence between the time of wetness frequency distribution in [2,6] and in [9].

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## 4.4. Source of errors

The reference collector with nickel-pigmented aluminium oxide absorber surface used in Rapperswil, Switzerland [2,6] had a non-airtight backside. The wind and rain loads may have had stronger impact than usual on the microclimate of the collector. This is the likely reason for shorter service lifetime estimates (19–23 years) compared to reference data from Zurich, Switzerland [9], which resulted in longer service lifetime estimates (23–26 years). The real expected service lifetime of  $C/Al_2O_3/Al$  absorber surfaces depends on the actual time of wetness frequency distribution of the collector microclimate during the years of operation at any given location. Additionally, the collector service lifetime depends very much on the control strategy of the microclimate inside the collector. With an airtight collector and controlled ventilation, longer lifetimes may be reached due to less condensation compared to a non-airtight collector and uncontrolled air ventilation.

Missing wavelength range between 1.1 and 2.5 µm caused some error in the optical measurements. The  $\alpha$  measurements done at HUT comply with the Uppsala University reference results within 0.5% (absolute) for the sample exposed to 6 h at 400°C (Fig. 2). Measurements comply within 1.7% for the sample exposed to 4 h at 80°C, 80% r.h. (Fig. 5). The PC value of this sample is 0.44, which well exceeds the limit value of 0.05. Therefore, it is likely that the error margin in  $\alpha$  measurements for samples with PC=0.05 (Fig. 3) is significantly smaller. Additionally, measuring the changes in  $\alpha$  instead of absolute values reduces the error margin as well. The  $\varepsilon$  measurements between the two universities comply within one percentage unit in all cases.

Some divergence in results may have been caused by small fluctuations in the climate chamber temperature and sample temperature during testing period combined with inhomogeneous microstructure of the samples. Requirement of temperature constancy for test panel cooling fluid is  $\pm 0.5^{\circ}$ C and flow should be over  $901 \text{min}^{-1}$  [5]. Due to technical restrictions in our tests, cooling fluid flow was less than  $901 \text{min}^{-1}$  thus increasing the temperature difference between the three samples. To minimize the effect, we accepted results only for the two samples nearest to the sample temperature sensor if the result of the third sample deviated from these significantly. Additionally, cooling flow temperature constancy exceeded temporarily  $\pm 0.5^{\circ}$ C during 300 and 400 h test periods. Due to running out of samples manufactured with identical parameters and simultaneous interruption in surface production, we could only test one unaged sample at 30°C. Supplemental tests were conducted at 30°C with naturally aged samples.

### 5. Discussion

Single glazed flat plate solar collectors utilizing  $C/Al_2O_3/Al$  absorber plates have been used in several countries for some 6 years now. Any visual changes of the surface resembling the change shown in Fig. 4 have not been reported so far by any of the owners.

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It is likely that during the hydration process, the thin graphite layer on the surface is oxidated through chemical reactions forming CO,  $CO_2$  and other compounds [12]. The revealed  $Al_2O_3$  layer subsequently follows the typical alumina-aluminium corrosion mechanisms.

Further improvements in the absorber structure could include use of antireflection coating, such as colloidal silica dipping AR coating [13,14]. If such a coating could be enhanced to act as a moisture barrier layer as well, it would add moisture resistance for very humid climates. However, the antireflection/moisture barrier coating needs to be inexpensive in order to keep the original  $C/Al_2O_3/Al$  absorber manufacturing concept simple and low cost.

#### 6. Conclusions

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Exposure tests at high temperature and moisture following the IEA SCH recommendations showed that the mechanically manufactured  $C/Al_2O_3/Al$  absorber surfaces mainly degrade through moisture-based hydration of aluminium oxide to pseudoboehmite and boehmite. The hydration process accelerates at higher temperatures with the presence of condensed water on the surface. High humidity alone without condensation at the same temperature is significantly less harmful. High operating temperatures at dry conditions alone do not deteriorate the surface.

Based on measured time of wetness of collector microclimate reference data, we estimated the service lifetime of the collector to be 19–26 years in normal use before the performance has degraded 5%. The collector service lifetime depends in practice significantly on the time of wetness frequency distribution and control strategy of the microclimate inside the actual collector. With an airtight collector and controlled ventilation, the service lifetime may be prolonged. Failures leading to increased humidity on the absorber surface present severe risk to absorber service lifetime.

#### Acknowledgements

This work was supported by the Finnish National Technology Agency (TEKES). The authors thank Dr. Tuquabo Tesfamichael from the Ångström Laboratory of the Uppsala University for the optical reference measurements.

#### References

- C.M. Lampert (Ed.), Failure and degradation modes in selected solar materials: a review, IEA SHCP Task X, 1989.
- [2] B. Carlsson, U. Frei, M. Köhl, K. Möller, Accelerated life testing of solar energy materials—case study of some selective materials for DHW systems, IEA SHCP Task X, 1994.
- [3] B. Carlsson, K. Möller, U. Frei, S. Brunold, M. Köhl, Sol. Energy Mater. Sol. Cells 61 (2000) 223–238.

- [4] S. Brunold, U. Frei, B. Carlsson, K. Möller, M. Köhl, Sol. Energy Mater. Sol. Cells 61 (2000) 239–253.
- [5] B. Carlsson, K. Möller, M. Köhl, U. Frei, S. Brunold, Sol. Energy Mater. Sol. Cells 61 (2000) 255–275.
- [6] S. Brunold, U. Frei, B. Carlsson, K. Möller, M. Köhl, Sol. Energy 68 (2000) 313-323.
- [7] P. Konttinen, P.D. Lund, R.J. Kilpi, Sol. Energy Mater. Sol. Cells 79 (2003) 273-283.
- [8] P. Konttinen, R.J. Kilpi, P.D. Lund, Thin Solid Films 425 (2003) 24-30.
- [9] M. Köhl, Renewable Energy 24 (2001) 597–607.
- [10] J. Halme, Reflectance measurement of solar selective surfaces with FTIR spectrometer and a DRIFT accessory, Special assignment report, Helsinki University of Technology, 2000, (in Finnish).
- [11] L.L. Shreir, R.A. Jarman, G.T. Burstein, Corrosion, Vol. 1, Butterworth and Heinemann, Oxford, 1995, p. 4:15.
- [12] L.H. Hihara, R.M. Latanision, Int. Mater. Rev. 39 (1994) 245-264.
- [13] T. Tesfamichael, A. Roos, Sol. Energy Mater. Sol. Cells 54 (1998) 213-221.
- [14] P. Nostell, A. Roos, B. Karlsson, Thin Solid Films 351 (1999) 170-175.