

## Integrating National Research Agendas on Solar Heat for Industrial Processes

### Project Deliverable 3.3: Industrial environment conditions for solar collector degradation

**D 3.3 – INDUSTRIAL ENVIRONMENT CONDITIONS FOR SOLAR COLLECTOR DEGRADATION: SURVEY ON RELEVANT DEGRADATION PARAMETERS AFFECTING THE DURABILITY AND PERFORMANCE OF SOLAR COLLECTOR COMPONENTS OPERATING UNDER INDUSTRIAL ENVIRONMENT CONDITIONS, INCLUDING MOST RELEVANT DEGRADATION PARAMETERS IN DIFFERENT INDUSTRIAL SECTORS**

<b>WP 3</b>	<b>TECHNOLOGY AND APPLICATIONS TO MEDIUM TEMPERATURE SHIP (150° - 400°)</b>
<b>Due date</b>	<b>31 December 2018</b>
<b>Submitted</b>	<b>17 September 2018</b>
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<b>GA Number</b>	<b>731287</b>
<b>Start of the project</b>	<b>01 January 2017</b>
<b>Duration of the project</b>	<b>48 months</b>

#### DISSEMINATION LEVEL

**PU** *Public*

#### NATURE OF THE DELIVERABLE

**R**

#### HISTORY

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## 1. Scope and Objectives

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The main objective of the INSHIP project is “acknowledging both the potential contribution of Solar Thermal technologies towards the development of sustainable industrial production and the need of a coordinated effort tackling the technological challenges still faced by these technologies when applied in industry. INSHIP aims at the definition of a European Common Research and Innovation Agenda (ECRIA) engaging major European research institutes, with relevant and recognized activities on SHIP into an integrated structure” (Horta et al.; 2016).

The Work Package 3 (WP3: Technology and applications to medium temperature SHIP (150°C to 400°C) “covers the research topics related to the development of technological solutions aiming at the integration of medium temperature technologies in SHIP applications” (Horta et al.; 2016).

Task 3.3 (Durability and Reliability) from WP 3 will focus on the research topics soiling and corrosion in industrial environment, enhanced reflectors and innovative automated cleaning processes.

Corrosion is one major degradation phenomenon that solar components for Concentrating Solar Power (CSP) collectors are bound to encounter during their service lifetime, especially at those sites near industrial environments, because it may seriously affect the optimal performance of materials. Therefore, the durability study of solar components (in particular reflectors) subjected to industrial atmospheres is a key subject that must be addressed. In this report, a revision of the most significant industrial environmental conditions that play a noteworthy role in solar collector degradation and the prominent parameters for their durability study are presented.

## 2. Terms and Definitions

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<b>Terms</b>	<b>Description</b>
CASS	Copper-accelerated acetic acid salt spray
CSP	Concentrating Solar Power
DIN	Deutsches Institut für Normung
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
NSS	Neutral salt spray
OPAC	Optical and aging characterization
PSA	Plataforma Solar de Almería
SHIP	Solar heat for industrial processes

### 3. Industrial environment conditions for solar collectors degradation

In this chapter, possible industrial environmental conditions for solar collector degradation and some classification schemes already published for other applications are reviewed.

One of the relevant pollutants that are involved in the corrosion of solar reflectors is H<sub>2</sub>S, among other reduced sulfur gases. Their main sources are organic decay processes, fossil fuel combustion and refining (Rice et al.; 1980). Marshes and volcanoes are other natural widely dispersed sources that contribute to the emission of this gas (Franey et al.; 1985). Also, pulp and paper industries suffer from indoor corrosion of this pollutant in their computerized control system (Watanabe et al.; 2006). As reported by Rice (1981), urban areas typically feature H<sub>2</sub>S concentrations of 1 µg/m<sup>3</sup> (0.00072 ppm), although much higher concentrations (34 µg/m<sup>3</sup>, 0.024 ppm) may be found where localized sources, such as paper mills, exist.

Although the environmental concentration of SO<sub>2</sub> has decreased in the last years thanks to the improvements achieved in the refining technology for reducing sulfur in fossil fuels (Watanabe et al.; 2006), SO<sub>2</sub> is still one of the most abundant gaseous contaminants from anthropogenic source, which is mainly caused by the combustion of sulfur-containing fossil fuels and the smelting of metal sulfide ores (Franey et al.; 1985; Leygraf and Graedel; 2000).

In addition, nitrogen oxides (principally as NO and NO<sub>2</sub>) are produced by the combustion of automotive fuels and fossil fuels in power stations (Syed; 2006). NO<sub>2</sub> is typically found at a concentration of 44 µg/m<sup>3</sup> (0.023 ppm) in urban centres (Rice; 1981) and its direct emission from traffic has increased in the last decades owing to modern diesel engines. In particular, nitric acid is one of its most stable forms in the atmosphere that may increase the corrosion of materials (Tidblad et al.; 2012).

International Electrotechnical Commission (IEC) established some limits for the maximum concentration values of SO<sub>2</sub> and H<sub>2</sub>S that are expected to be found in polluted environments at different levels (Table 1) (Hillman et al.; 2007). As can be observed in this table, industrial environments are the most aggressive ones, reaching values up to 15.3 ppm for SO<sub>2</sub> and 28.5 ppm for H<sub>2</sub>S. Concentrations included in this table are highly valuable because they must be considered in the different types of polluted environments to avoid locations with higher values.

Table 1. IEC classifications for chemically active substances (values in ppm, parts per million).

Pollutant	Clean room	Controlled environment	Rural	Heavy urban or industrial	Adjacent to industrial	Inside industrial
SO <sub>2</sub>	0.038	0.038	0.038	0.4	3.8	15.3
H <sub>2</sub> S	0.001	0.004	0.004	0.2	4.1	28.5

Table 2 shows the outdoor and indoor concentration ranges of the most significant atmospheric contaminants (H<sub>2</sub>S, SO<sub>2</sub>, NO<sub>2</sub>) that are subject to study (Leygraf; 2007).

Table 2. Outdoor and indoor concentration ranges (ppbv, parts per billion per volume) of the most prevalent pollutant gases in atmospheric corrosion (Leygraf; 2007).

Pollution level	H <sub>2</sub> S (ppbv)	SO <sub>2</sub> (ppbv)	NO <sub>2</sub> (ppbv)
Outdoor	0.5-25	1-70	10-80
Indoor	0.1-0.7	0.3-15	1-30

Finally, Table 3 summarizes the main industrial sectors that are responsible for the emissions of these corrosive gases (Perry and Green; 1999). The information included in this table permits to identify the main corrosive gases present in the different industrial sectors and consequently, the potential degradation factors for the solar collectors installed in such environments. The following section includes a survey about the most relevant degradation mechanisms appearing due to the mentioned gases.

Table 3. Main industrial sources of the most prevalent pollutant gases (Perry and Green; 1999).

Pollutant	Industrial source
SO <sub>2</sub>	Use of coal and oil, industrial plants (cement, coke, incinerators)
NO <sub>2</sub>	Traffic, cement plants, incinerators
H <sub>2</sub> S	Pulp and paper industry, farming, coal-preparation plants, coke plants
Cl <sub>2</sub>	Pulp and paper industry

## 4. Relevant degradation parameters affecting the durability of solar collector components under industrial environment conditions

This chapter presents a concise literature revision on the typical degradation parameters of industrial environments which are likely to affect the durability and performance of solar collector components.

The study of the atmospheric corrosion of materials has been mainly devoted to pure metals and alloys and special attention has been paid to the influence of typical industrial environments on electrical contact materials, such as silver, copper, zinc, iron, etc. (Abbot; 1974). Franey and Graedel (1985) revised the synergistic effects of atmospheric corrosive gases on metals and alloys (Franey and Graedel; 1985), whereas Steppan et al. (1987) focused the investigations on the corrosion failure mechanisms during accelerated aging tests of pure silver, copper, and aluminum used in microelectronic devices (Steppan et al.; 1987).

Among the multiple gaseous pollutants that are present in an industrial atmosphere, hydrogen sulfide ( $\text{H}_2\text{S}$ ), sulfur dioxide ( $\text{SO}_2$ ), nitrogen dioxide ( $\text{NO}_2$ ) and chlorine ( $\text{Cl}_2$ ) are the prevailing corrosive agents of the metallic parts of a solar collector, including the reflective layers of the mirrors. For this reason, one representative industrial environment for general use in accelerated aging was set at 200 ppb  $\text{H}_2\text{S}$ , 200 ppb  $\text{SO}_2$ , 200 ppb  $\text{NO}_2$ , 90% RH at 30-60°C, which appeared to give acceleration factors on the order of 30 to 40 times if comparing to typical industrial environments (Abbot; 1974). Such high humidity values are justified by the fact that water vapor forms thin aqueous films on the surface of metals (Franey and Graedel; 1985), which act as a medium for the absorption of atmospheric gases and the following dissolution of metals, especially of solid silver (Graedel; 1992). It has been found that the corrosion rate of silver is enhanced by humidity, whether the main (or unique) pollutant is  $\text{SO}_2$  (Kleber et al.; 2007) or  $\text{H}_2\text{S}$  (Kim; 2003). In the case of aluminum, the  $\text{SO}_2$  adsorbed on its surface depends on the humidity content of the atmosphere, which causes the formation of sulfuric acid and thus accelerates the attack of its natural protection layer (de la Fuente et al.; 2007).

The main cause of silver corrosion is sulfidation (Volpe and Peterson; 1989), especially by reduced sulfur gases including  $\text{H}_2\text{S}$ , sulfur vapor, and mercaptans (Rice et al.; 1980). Besides,  $\text{NO}_2$  can play an important role in the sulfidation rate of silver with  $\text{H}_2\text{S}$ , considering its relative higher abundance in the atmosphere than  $\text{H}_2\text{S}$  (Volpe and Peterson; 1989; Kim; 2003). Reduced sulfur pollutants have also been reported to corrode copper (Johansson and Leygraf; 1999) and accelerate stress corrosion cracking of steel (Rice et al.; 1980). Conversely, aluminum is quite unreactive to reduced sulphur compounds (Graedel; 1989) and initially it was noted its resistance to atmospheric  $\text{SO}_2$  if compared with other metals such as iron and zinc (Sydberger and Vannerberg; 1972). Actually, ozone ( $\text{O}_3$ ),  $\text{SO}_2$ ,  $\text{NO}_2$  and the deposition of chlorides have been found to strongly influence aluminum corrosion, as well as humidity and the pH in rain (Syed; 2006; Morcillo et al.; 2012).  $\text{SO}_2$  (alone or in combination with other corrosive gases and salinity) has been reported to promote major degradation on metals (Carlsson et al.; 2000) and more precisely on the metallic parts of the absorbers and reflectors used in CSP technologies (Slamova et al.; 2016).

Few other authors devoted their investigations on studying the effects of polluted atmospheres on solar reflectors and other CSP components. The interaction between pollutant gases (including  $\text{SO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{NO}_2$ ) and silvered polymer reflectors has been previously described (Schissel and Czanderna; 1980). Moreover, the influence of moist acid vapors (i.e.  $\text{H}_2\text{S}$ ,  $\text{HCl}$ ) was studied on 22

different second-surface glass mirrors (Coyle et al.; 1982), neutral salt spray (NSS) and copper-accelerated acetic acid salt spray (CASS) tests were performed on silvered glass reflectors (Schütz et al.; 1997) and moist SO<sub>2</sub> atmospheres were tested on absorber coatings (Köhl; 2001) and on aluminum reflectors (Almanza and Martínez; 2012). Finally, the optical and aging characterization (OPAC) laboratory (a Spanish-German joint research group at the Plataforma Solar de Almería, PSA) has also thoroughly investigated the corrosion mechanisms of solar reflectors exposed to a wide range of aggressive atmospheres (Sutter et al.; 2014; Sutter et al.; 2015; Wette et al.; 2016), including industrial environments (Fernández-García et al.; 2014; García-Segura et al.; 2018).

It should be noted that salt spray tests (ISO 9227:2017; 2017), as well as Kesternich tests (ISO 6988:1985; 1985; DIN 50018; 1997), are common test methods for industrial applications that are normally applied within the testing plan for international projects and services to industries, but they do not concern the effect of dry deposits. In contrast, other tests are available to simulate such conditions (IEC 60068-2-43:2003; 2003; IEC 60068-2-42:2004; 2004; IEC 60068-2-60:2016; 2016; ISO 10062:2006; 2006). Whereas IEC 60068-2-43:2003 and IEC 60068-2-42:2004 are devoted to the influence of single pollutants (H<sub>2</sub>S and SO<sub>2</sub>, respectively) at relatively high concentrations (up to 25 ppm), IEC 60068-2-60:2016 studies the synergism of various gaseous species (H<sub>2</sub>S, SO<sub>2</sub>, NO<sub>2</sub>, Cl<sub>2</sub>) at lower concentrations (0.01-0.5 ppm). ISO 10062:2006 considers both the single-pollutant and the gas mixture cases, at concentrations in the range of 0.02-0.5 ppm. These standards were initially conceived for the testing of electronic components including copper, gold, silver and other noble metals and alloys, but they may be applied to solar collector components because of the metallic parts that they contain.



## 5. Classification of exposure sites according to the corrosion level

The classification of exposure sites according to their corrosivity level is described in the ISO 9223 standard (ISO 9223:2012; 2012). The procedure to evaluate the corrosivity level of an outdoor site is as follows. First, three coupons (replicate samples) of each type of metal (aluminum, copper, steel, zinc) are properly identified and weighed in a precision scale (three or four decimals). They must be exposed on site for one year. After that, they are collected and the following number of cleaning steps is applied before being weighed.

1. The first step is a mechanical cleaning with a soft-bristle brush under running deionized water in order to remove the slightly adhered artifacts or voluminous corrosion products. The ideal procedure should eliminate only the corrosion products and no material of the base metal. To confirm this, a control coupon is necessary. The control coupons (not corroded or fresh) must be cleaned by the same procedure of the testing coupons, weighing them before and after cleaning. At least three-decimal weighing is recommended to precisely determine the metal loss resulting from the cleaning method. The preferred cleaning method will be the one which efficiently removes the corrosion products and also produces a low or nonexistent mass loss when applied to the control coupons.
2. The second step is a chemical cleaning, which is detailed in Table 4. To improve the chemical cleaning, a concurrent ultrasonic bath treatment is recommended. Coupons must be vertically immersed in the corresponding solutions at ambient temperature (20-25°C). The total immersion time can be variable, depending on necessity, and one-liter solution is recommended for each three-coupon batch of metals and for each exposure site.

Table 4. Metals, chemical products and recommended conditions for the chemical cleaning in each case (according to ISO 8407:2009; 2009).

Material	Chemicals	Total time	Temperature	Notes
Aluminum and alloys	Nitric acid (HNO <sub>3</sub> , ρ = 1.42 g/ml)	1-5 min	20-25°C	To avoid excessive stripping of the base metal, bulky artifacts must be removed
Copper and alloys	50 g amidosulfonic acid (sulfamic acid), distilled water up to 1000 ml	5-10 min	20-25°C	-
Iron and steel	500 ml hydrochloric acid (HCl, ρ = 1.19 g/ml), 3.5 g hexamethylenetetramine, distilled water up to 1000 ml	10 min	20-25°C	The removal of artifacts may be increased or higher times may be employed
Zinc and alloys	250 g glycine (NH <sub>2</sub> CH <sub>2</sub> COOH), distilled water up to 1000 ml (saturated solution)	1-10 min	20-25°C	Glycine is low soluble in water and easily precipitates at room temperature, therefore a magnetic mixer is recommended

After the chemical cleaning, the coupons must be carefully brushed and rinsed with deionized water and then with ethanol. They must be dried in a muffle furnace at 50°C for 5 min and cooled down in a desiccator at ambient temperature before being weighed. The scale must be properly calibrated and placed in a room with no air current. The calculation of the corrosion rate is as follows:

$$r_{corr} = \frac{\Delta m}{A \cdot t}$$

Where:

- $r_{corr}$ : corrosion rate [ $\text{g}/(\text{m}^2 \cdot \text{a})$ ].
- $\Delta m$ : corrosion mass loss [g].  $\Delta m$  is the result of subtracting the total mass loss (from the initial and final weighing of coupons) and the material loss due to mechanical cleaning.
- $A$ : coupon surface [ $\text{m}^2$ ].
- $t$ : exposure time [years].

Once the corrosion rates are determined, the corrosivity levels are calculated according to Table 5. There are six possible corrosion categories. C1 is very low, C2 is low, C3 is medium, C4 is heavy, C5 is very heavy and CX is extreme corrosion levels.

Table 5. Corrosion rates ( $r_{corr}$ ) of metals and their corresponding corrosion categories (according to ISO 9223:2012; 2012).

Corrosion category	Corrosion rates of metals ( $r_{corr}$ )				
	Unit	Unalloyed steel	Zinc	Copper	Aluminum
C1	$\text{g}/(\text{m}^2 \cdot \text{a})$	$r_{corr} \leq 10$	$r_{corr} \leq 0.7$	$r_{corr} \leq 0.9$	negligible
	$\mu\text{m}/\text{a}$	$r_{corr} \leq 1.3$	$r_{corr} \leq 0.1$	$r_{corr} \leq 0.1$	-
C2	$\text{g}/(\text{m}^2 \cdot \text{a})$	$10 < r_{corr} \leq 200$	$0.7 < r_{corr} \leq 5$	$0.9 < r_{corr} \leq 5$	$r_{corr} \leq 0.6$
	$\mu\text{m}/\text{a}$	$1.3 < r_{corr} \leq 25$	$0.1 < r_{corr} \leq 0.7$	$0.1 < r_{corr} \leq 0.6$	-
C3	$\text{g}/(\text{m}^2 \cdot \text{a})$	$200 < r_{corr} \leq 400$	$5 < r_{corr} \leq 15$	$5 < r_{corr} \leq 12$	$0.6 < r_{corr} \leq 2$
	$\mu\text{m}/\text{a}$	$25 < r_{corr} \leq 50$	$0.7 < r_{corr} \leq 2.1$	$0.6 < r_{corr} \leq 1.3$	-
C4	$\text{g}/(\text{m}^2 \cdot \text{a})$	$400 < r_{corr} \leq 650$	$15 < r_{corr} \leq 30$	$12 < r_{corr} \leq 25$	$2 < r_{corr} \leq 5$
	$\mu\text{m}/\text{a}$	$50 < r_{corr} \leq 80$	$2.1 < r_{corr} \leq 4.2$	$1.3 < r_{corr} \leq 2.8$	-
C5	$\text{g}/(\text{m}^2 \cdot \text{a})$	$650 < r_{corr} \leq 1500$	$30 < r_{corr} \leq 60$	$25 < r_{corr} \leq 50$	$5 < r_{corr} \leq 10$
	$\mu\text{m}/\text{a}$	$80 < r_{corr} \leq 200$	$4.2 < r_{corr} \leq 8.4$	$2.8 < r_{corr} \leq 5.6$	-
CX	$\text{g}/(\text{m}^2 \cdot \text{a})$	$1500 < r_{corr} \leq 5500$	$60 < r_{corr} \leq 180$	$50 < r_{corr} \leq 90$	$r_{corr} > 10$
	$\mu\text{m}/\text{a}$	$200 < r_{corr} \leq 700$	$8.4 < r_{corr} \leq 25$	$5.6 < r_{corr} \leq 10$	-

## 6. Conclusions

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A number of conclusions can be drawn from this deliverable, and they are summarized in the following list:

- The most significant atmospheric contaminants that may act as corrosive agents of the metallic parts of solar collectors are  $H_2S$ ,  $SO_2$ ,  $NO_2$  and  $Cl_2$ .
- Anthropogenic emissions of  $H_2S$  (and  $Cl_2$ ) are mainly produced by the pulp and paper industry and by refining processes,  $SO_2$  emissions principally come from the combustion of sulfur-containing fossil fuels and atmospheric  $NO_2$  proceeds from the combustion of automotive and fossil fuels.
- The study of the atmospheric corrosion of materials has been up to date mainly devoted to pure metals and alloys, such as silver, copper, zinc, iron, etc.
- The ambient humidity acts as a medium for the absorption/adsorption of atmospheric gases on the metals surfaces and their subsequent dissolution.
- The main cause of silver corrosion is sulfidation by  $H_2S$ , while  $O_3$ ,  $SO_2$ ,  $NO_2$  and the deposition of chlorides have been found to strongly influence aluminum corrosion.
- Few authors have studied the effects of polluted atmospheres on solar reflectors and other CSP components.
- The corrosivity of the site must be determined according to the existing ISO 9223 standard.

## 7. Appendix

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