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Effects of reduced sulphur atmospheres on reflector materials for concentrating solar thermal applications

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ABSTRACT

The degradation of reflector materials for concentrating solar thermal applications is analysed. Corrosion of their metallic reflective layer is considered a major problem in facilities which are located near industrial sites, where reduced sulphur gases may be present. Accelerated ageing tests were performed to study the influence of H₂S on the corrosion of two types of silvered glass reflectors and one aluminium reflector. Different degradation patterns were found for silvered glass reflectors, whereas aluminium reflectors did not corrode in the presence of the sulphurous gas. Therefore, industrial pollution caused by this type of gas may decrease the solar collectors' performance.

1. Introduction

The problematic question related with energy in our present-day society has been and still is of major concern. To tackle it, a significant number of renewable energy technologies have been developed around the world in the last decades [1]. One of the most preeminent and feasible solutions to this worldwide issue is the implementation of plants using concentrating solar thermal technologies (also named concentrating solar power, CSP, plants) [2]. Actually, this kind of technology has experienced a widespread advancement in many countries, led by Spain and USA [3]. Today around 5 GW_{electric} of CSP capacity is installed worldwide, almost half of it deployed in Spain. The 50 power plants in Spain represent around 3% of the Spanish electricity generation mix. CSP has reached now an electricity generation cost of 14 c€/kWh at relatively good sunny places, and with increasing installed capacity a large potential of further cost reduction is foreseen [4].

A CSP facility is integrated by different components including receivers, heat transfer fluids and reflectors. The last ones constitute a large percentage of the total surface of the solar plant and are expected to comply with a high optical performance along their service lifetime (aimed at 10–30 years or more) under demanding environmental conditions [5]. The durability of solar reflectors is one of the crucial factors in the proper operation of any CSP facility. The plants are sometimes located near industries affected by heavily polluted atmospheres, which

may give a boost to the corrosion of solar reflectors. Among the most frequent corrosive gases found in the surroundings of industrial sites, hydrogen sulphide (H₂S), sulphur dioxide (SO₂), nitrogen dioxide (NO₂), and chlorine (Cl₂) are considered to be very harmful [6]. In particular, elevated levels of reducing sulphur-based gases (H₂S, sulphur vapour, and mercaptans) are common in a wide range of different industrial environments, such as rubber manufacturing, sewage and waste-water treatment plants, petroleum refineries, coal-generation power plants, pulp and paper mills, and many others from anthropological sources [6–11]. Furthermore, hydrogen sulphide is known to be extremely corrosive to most metals and alloys [12]. For this reason, it is considered to be a target gas to study the durability of solar reflectors facing corrosive atmospheres. Historically, the major problem with this gas has been the general lack of published data, due to the difficulties in obtaining reliable measurements [9]. However, International Electrotechnical Commission (IEC) environmental guidelines for controlled environments classify different types of atmospheres according to their content in chemically active substances including H₂S [13]. The typical concentrations of this gas for different atmospheric environments are reported in [6] as 0.6 ppb for clean rooms, 4 ppb for both controlled and rural environments, 200 ppb for urban sites with heavy traffic or industrial facilities, 4075 ppb for places adjacent to industries and 28500 ppb for indoor industrial atmospheres.

Among the different types of concentrating solar reflectors, back-silvered glass reflectors are the most deployed ones. They are classified

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Nomenclature		EDS	Energy dispersive X-ray spectroscopy
Acronyms		Symbols	
CSP	Concentrating solar power	T	Temperature
PVD	Physical vapour deposited	RH	Relative humidity
IEC	International electrotechnical commission	pp	Percentage point
XPS	X-ray photoelectron spectroscopy	N	Number of corrosion defects
SEM	Scanning electron microscopy		

as second-surface reflectors because they are based on a thin reflective silver layer which is protected by a 1–4 mm glass substrate on the front side and typically a copper layer and several protective paints on the back side. On the other hand, aluminium reflectors are usually used in small-scale applications, e.g. process heat [14]. They are first-surface reflectors composed of a physical vapour deposited (PVD) aluminium layer, which is applied on an aluminium substrate. Transparent SiO_2 -based sol-gel coatings are used to protect the reflective aluminium layer [15]. Therefore, solar reflectors contain metal sheets and films that are liable to be corroded in an environment polluted by sulphur.

In the particular case of the silver sulphidation, its corrosion rate is dominantly dependent on the reduced sulphur pollutant concentration. The presence of oxidising species, such as NO_2 , Cl_2 , HCl , O_3 , $\text{O}_2\text{-H}_2\text{O}$, has been considered to increase it as well [16–18]. The main reaction product of the sulphurous corrosion of silver is silver sulphide (Ag_2S), a monoclinic crystal also known as argentite or acanthite [6,19]. In those environments slightly polluted with H_2S , compounds such as sulphates, chlorides [20], and nitrates can be found on the silver surface, whereas Ag_2S is found to be the preminent silver-containing substance when

silver is mostly exposed to H_2S [21]. In the case of copper, complex copper hydroxides, sulphates, carbonates, and chlorides have been found as the main corrosion products on outdoor exposures, where SO_2 , H_2S , and O_3 are considered to have a significant influence in copper corrosion [7,9]. As for aluminium, Graedel [22] did a thorough review of the corrosion mechanisms involved in the atmospheric exposure of this metal and found that reduced sulphur compounds were not essential in its corrosion chemistry. Conversely, aluminium has been proven to be more reactive when exposed to marine environments containing chlorides and to atmospheres with sulphur dioxide [22,23].

Much research has been focused on the effects that industrial air atmospheres may have on electrical contact materials under laboratory accelerated conditions [24,25]. Consequently, a great number of experiments combining different corrosive gases were designed and applied to silver and copper, and their correspondent reaction products were analysed. H_2S was found to be essential in such environments [26], along with combinations of SO_2 and NO_2 and other atmospheric factors (O_2 , H_2O , chlorides), which were responsible for the oxidation of H_2S and thus providing a reducing source of free sulphur [18]. Other

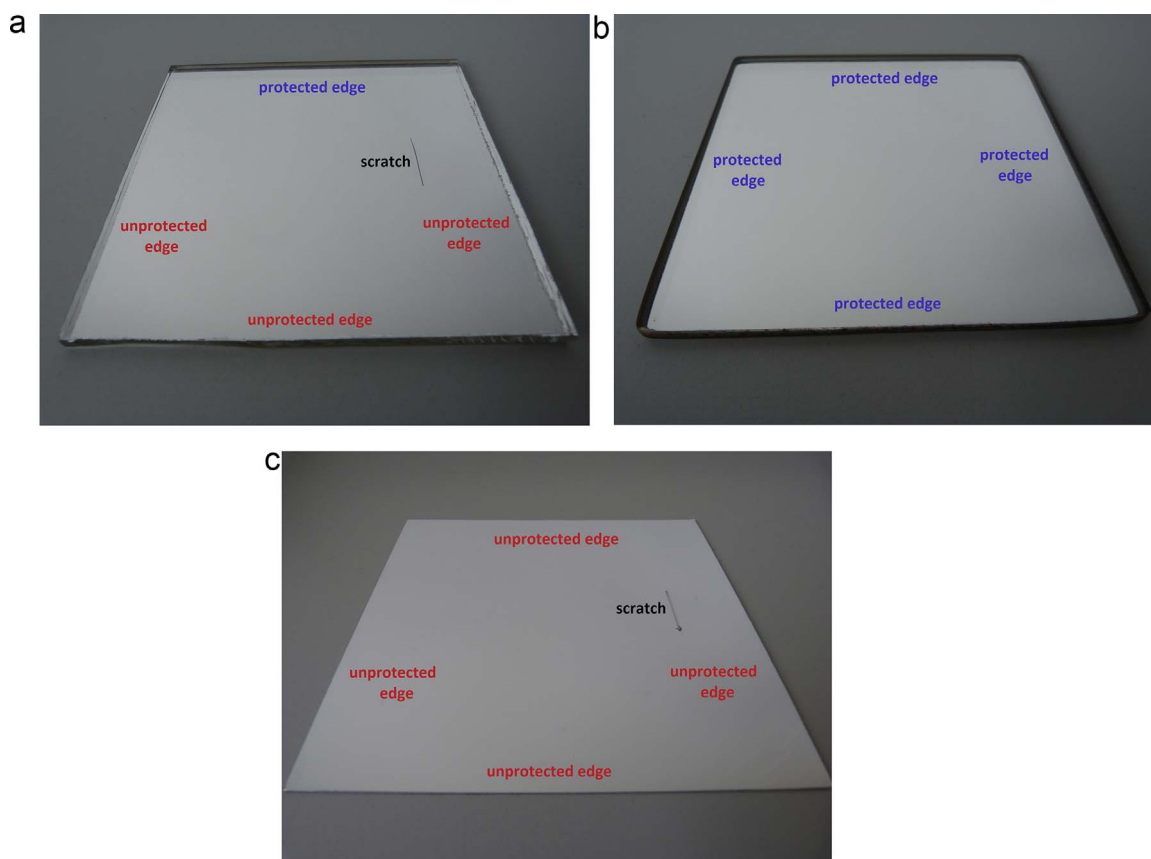


Fig. 1. Overview of the samples tested: silvered glass reflector type 1 with one protected edge, three unprotected edges and one scratch (a), silvered glass reflector type 2 with four protected edges (b) and aluminium reflector with four unprotected edges and one scratch (c). The protected edges are labelled in blue, the unprotected edges in red and the scratch in black. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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