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TASK III

PERFORMANCE TESTING OF SOLAR COLLECTORS

Environmental Factors of Collector Degradation

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TASK III

Performance testing of solar collectors

ENVIRONMENTAL FACTORS
OF
COLLECTOR DEGRADATION

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Task III: Performance Testing of Solar Collectors

Subtask F: Development of a Basis for Identifying the Performance Requirements and for Predicting the Service Life of Solar Collector System Components

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INTRODUCTION TO THE INTERNATIONAL ENERGY AGENCY AND THE IEA SOLAR HEATING AND COOLING PROGRAMME

The International Energy Agency was formed in November 1974 to establish cooperation among a number of industrialized countries in the vital area of energy policy. It is an autonomous body within the framework of the Organization for Economic Cooperation and Development (OECD). Twenty-one countries are presently members, with the Commission of the European Communities also participating in the work of the IEA under a special arrangement.

One element of the IEA's programme involves cooperation in the research and development of alternative energy resources in order to reduce excessive dependence on oil. A number of new and improved energy technologies which have the potential of making significant contributions to global energy needs were identified for collaborative efforts. The IEA Committee on Energy Research and Development (CRD), supported by a small Secretariat staff, is the focus of IEA RD&D activities. Four Working Parties (in Conservation, Fossil Fuels, Renewable Energy, and Fusion) are charged with identifying new areas for cooperation and advising the CRD on policy matters in their respective technology areas.

Solar Heating and Cooling was one of the technologies selected for joint activities. During 1976-77, specific projects were identified in key areas of this field and a formal Implementing Agreement drawn up. The Agreement covers the obligations and rights of the Participants and outlines the scope of each project or "task" in annexes to the document. There are now eighteen signatories to the Agreement:

Australia
Austria
Belgium
Canada
Denmark
Commission of the European Communities
Finland
Federal Republic of Germany
Greece (withdrew in 1986)
Italy
Japan
Netherlands
New Zealand
Norway
Spain
Sweden
Switzerland
United Kingdom
United States

The overall programme is managed by an Executive Committee, while the management of the individual tasks is the responsibility of the Operating Agents. The tasks of the IEA Solar Heating and Cooling Programme, their respective Operating Agents, and current status (ongoing or completed) are as follows:

Task I	Investigation of the Performance of Solar Heating and Cooling Systems - Technical University of Denmark (Completed).
Task II	Coordination of Research and Development on Solar Heating and Cooling - Solar Research Laboratory - GIRIN, Japan (Completed).
Task III	Performance Testing of Solar Collectors - University College, Cardiff, U.K. (Ongoing).
Task IV	Development of an Insulation Handbook and Instrument Package - U.S. Department of Energy (Completed).

Task V	Use of Existing Meteorological Information for Solar Energy Application - Swedish Meteorological and Hydrological Institute (Completed).
Task VI	Performance of Solar Heating, Cooling, and Hot Water Systems Using Evacuated Collectors - U.S. Department of Energy (Ongoing).
Task VII	Central Solar Heating Plants with Seasonal Storage - Swedish Council for Building Research (Ongoing).
Task VIII	Passive and Hybrid Solar Low Energy Buildings - U.S. Department of Energy (Ongoing).
Task IX	Solar Radiation and Pyranometry Studies - Deutscher Wetterdienst Meteorologisches Observatiurm, FRG (Ongoing).
Task X	Materials Research & Testing - Solar Research Laboratory, GIRIN, Japan (Ongoing).
Task XI	Passive Solar Commercial Buildings - Swiss Federal Office of Energy (Ongoing).

TASK III
PERFORMANCE TESTING OF SOLAR COLLECTORS

The overall goal of Task III is by international cooperation to develop and validate common test procedures for rating the performance of solar thermal collectors and solar domestic hot water heating systems.

Task III was initiated in 1977 with three subtasks:

Subtask A: Standard Test Procedures to Determine Thermal Performance

Subtask B: Development of Reliability and Durability Test Procedures

Subtask C: Investigation of the Potential of Solar Simulators

Upon the completion of these subtasks at the end of 1982, the Executive Committee approved an extension of the Task with the following three subtasks:

Subtask D: Characterization of the Thermal Performance of Solar Collectors

Subtask E: Development of a Capability to Evaluate Domestic Hot Water System Performance using Short-Term Test Methods

Subtask F: Development of a Basis for Identifying the Performance Requirements and for Predicting the Service Life of Solar Collector System Components

At the end of 1985 a further extension was approved, with a completion date at the end of 1987.

Participants in Task III (those marked * until the end of 1985 only) are: Australia*, Austria*, Belgium*, Canada, Denmark, F.R.Germany, Italy, Japan*, the Netherlands, Spain, Sweden, Switzerland, United Kingdom, United States and the Commission of the European Communities.

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EXECUTIVE SUMMARY

This report is concerned with the forms of material degradation which affect the reliability and durability of solar thermal collectors.

The terms "reliability" and "durability" both refer to a resistance to failure in the operating characteristics of the collector, but the failures referred to are generally sudden and more-or-less complete breakdown in the first case and a slow gradual deterioration of performance in the second.

The problems of the reliability of solar collectors usually have to do with the structural integrity of the collector, while durability is more often a materials problem. The distinction is not clear-cut, however, since the breakdown of thermal insulation material, for example, can be be both sudden and catastrophic, and therefore affect the reliability of the collector.

The report reviews the forms of material degradation observed in solar thermal collectors and the factors of the internal environment of the collector (moisture, ultraviolet radiation, etc.) which are the main causes of degradation. An account is then given of the methods used to quantify and measure both the degradation and the environmental factors which affect the degradation.

The ability to measure degradation and environmental variables makes it possible to specify test procedures and minimum standards for the durability of collector components, and a discussion of these is given.

Following a brief review of recent studies of the internal environment of collectors, the report then concludes with recommendations for future work aimed at providing information about the best choice of materials and design to minimize the effects of degradation.

This report is intended as a contribution to the cooperation between test engineers and materials scientists in their overall objective of optimizing the long-term durability and cost-effectiveness of solar collectors.

1 INTRODUCTION

1.1 Reliability and durability of solar thermal collectors

Whether solar heating systems are economic is determined on the one hand by the capital costs of construction and installation of systems, and on the other hand by the lifetime of their components and the cost of maintenance. The most critical component of the system from the point of reliability and durability is usually the collector array, since this is subjected to the extremes of the outdoor environment.

The failure modes that affect the reliability and durability of solar collectors have been identified in a number of studies, either from stagnation tests or by inspection of systems in operation [1] - [6]. They range from dirt on the covers through structural defects to breakdown of the collector materials.

1.1.1 Dirt on collector covers

Soiling of the outside of a cover by dust and dirt is not usually a serious problem. Except in particularly dusty or smoky environments or if the collector is at a shallow angle of tilt, the cleaning action of rain or snow prevents an appreciable build-up. Then soiling of the cover tends to diffuse rather than attenuate the solar radiation. With some plastic materials, however, the adhesion of dirt is strengthened by electrostatic effects, and regular washing is needed to maintain the cover transparency [1].

1.1.2 Structural failures

Structural failures are usually serious because they result in some form of leakage into or out of the collector. They may be due to faults in the collector construction, such as an ill-fitting gasket, but more often occur during operation as a result of environmental stress which the collector is not able to withstand. An example is the cracking of glass covers under thermal stress, under snow or wind loading, or due to the impact of hail.

Apart from their influence on material degradation, soiling and water contamination of the inside of the collector have a direct effect on the collector performance: dirt on the inside of the cover or the absorber plate reduces the optical efficiency; condensation on the inside surfaces of the collector absorbs latent heat and reduces the thermal efficiency; and waterlogging reduces the effectiveness of thermal insulation. Moisture and soiling together may encourage the growth of algae or fungi, which cause further deterioration.

Reliability studies have identified the causes of these failures, and recommendations have been drawn up on the means of avoiding them [4]. Second-generation collectors employ materials and manufacturing processes that are designed to provide a more robust construction. To ensure that a collector is sufficiently sound, many different qualification tests have been developed, and these are the subject of a separate Task III technical report [7].

1.1.3 Material degradation

Material degradation is normally a slow process which at first has an imperceptible effect on collector performance. Examples include the embrittlement or opacity of plastics, structural or chemical changes to absorber coatings, and the corrosion of metal components. Material degradation is important, however, because as a rule it ultimately leads either to a significant deterioration of performance or to catastrophic mechanical breakdown. In the well-designed solar collector, therefore, material degradation is the factor which limits the durability.

1.2 Purpose of report

Durability studies have given much qualitative information on the forms of material degradation that can occur in solar collectors, but without quantitative information on the physical environment experienced by the different components of the collector it is not possible to predict the rate of material degradation or to make recommendations on how to limit it. It is the purpose of this report, therefore, to indicate the factors which are responsible for material degradation of solar collector components, and to describe methods commonly used to quantify and measure them. The aim is to enable solar engineers to fully characterize the internal environment of solar collectors, as a basis both for improving collector design and for seeking advice from materials experts.

1.3 References

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2 DEGRADATION OF COLLECTOR MATERIALS

2.1 Cover materials

2.1.1 Materials used for collector glazing

Glass is a widely-used cover material, which is highly resistant to degradation by radiation and chemical attack. Two types are used for collector glazing:

- float glass,

and

- low-iron glass.

Because glass is brittle, heavy and relatively expensive, however, many different plastic materials have also been used for collector glazing. These include (Trade names are given only as examples.):

- polycarbonate (PC) - 'Lexan' 'Qualex'
- poly(ethylene terephthalate) (PET) - 'Mylar'
- poly(methyl methacrylate) (PMMA) - 'acrylic' 'Perspex' 'Plexiglas'
- polytetrafluoroethylene (PTFE) - 'Teflon'
- poly(vinyl chloride) (PVC) - 'Novolux'
- poly(vinyl fluoride) (PVF) - 'Tedlar'
- cellulose acetate-butyrate (CAB) - 'butyrate' 'Uvex'
- perfluoro(ethylene-propylene) copolymer (FEP) - 'Teflon FEP'
- (glass-)fibre-reinforced polyester (GRP, FRP) - 'Filon' 'Malaray' 'Sun-lite' 'Cristal'
- laminated acrylic/polyester - 'Flexigard'

Plastic materials are generally more susceptible to material degradation under the operating conditions of solar collectors.

2.1.2 Failure modes of glass covers

Failure modes for glass include:

- breakage
- abrasion
- (chemical) weathering

Breakage is self-explanatory. It may be caused by impact, including vandalism, or it may be caused by thermal stress due to differential expansion or to direct contact with hot metal supports or glazing bars.

Abrasion refers to scratching by dust or grit: a physical weathering process which is accelerated by the influence of wind and rain.

The chemical weathering of several glasses considered for solar applications was studied by Shelby, Vitko and Pantano [1] using accelerated test methods. Only window glasses (soda-lime silicates) showed any significant weathering.

The chemical weathering of window glasses (soda-lime silicates) is a two-stage process involving diffusion of sodium (and sometimes of alkaline-earth metals) from the glass into a surface water film and of protons from the water into the glass, followed by an erosion of the surface due to thermal stress or cycles of wetting and dehydration. The etching of the surface and the build-up of powdery deposits on the surface cause a loss in the transmittance of the glass.

Shelby, Vitko and Pantano stress that the accelerated test results should not be taken as an indication that window glasses are unsuitable for solar applications: under normal ambient conditions their rate of weathering is negligible.

2.1.3 Degradation of cover glass

No serious material degradation of glass collector covers was reported in any of the inspections of solar installations [2] - [6]. For the types of glass normally used in solar collectors weathering is clearly not a significant problem.

(Note: In contrast with the absence of material degradation in glass covers, the breakage of these covers is quite common. In the CEC survey of 85 systems, for example, two thirds of the installations had glass covered collectors, and of these 27% had at least one broken cover. The most common cause of breakage was identified as thermal stress.)

2.1.4 Failure modes of plastic covers

The principal forms of deterioration in polymeric cover materials are:

- discoloration
- abrasion
- corrosion
- embrittlement
- softening
- warping
- shrinkage
- crazing and cracking
- fibre separation
- delamination

The term 'discoloration' applied to transparent cover materials refers to what is in fact a coloration and/or opacity of the material. A familiar example is the 'after-yellowing' of GRP.

Abrasion, caused by the combined effects of wind and dust, and corrosion, due to chemical or biological attack, are two forms which an erosion of plastic surfaces can take. The most commonly observed form of corrosion of covers is 'chalking', the formation of a dry, white powdery surface. This is caused by the evaporative deposition of solids leached out of the cover by volatile outgassing products.

Discoloration, erosion, or the condensation onto the glazing of opaque outgassing products from the insulation or sealants can each affect the optical properties of the glazing, either by reducing its transmittance or, less importantly, by diffusing the incident radiation.

Embrittlement and softening are changes of mechanical properties which, like discoloration, generally follow modifications of the chemical bonding in the material. Heat may be a direct cause of softening, especially in polymers such as PMMA, PVC or CAB where the temperatures attained in operation (up to 100 °C) can approach the softening point of the material.

Warping describes deformations of the material such as 'doming' - where the glazing bows outwards - or 'dishing' - where it sags. A cover that has softened becomes susceptible to stretching because of creep under its own weight, and this can lead to sagging, collapse, and eventually to the onset of permanent set. Warping of covers can also occur as a direct result of thermal expansion.

Shrinkage due to aging (as opposed to 'mould shrinkage') is increased by dry conditions and high temperatures. It can result in the loosening of covers and hence a loss of air- or water-tightness.

Crazing is a stress-induced network of fissures in the surface of the material. In solar-collector covers the stresses are usually due to thermal cycling. The crazes are nucleated at microcracks formed in the material during manufacture, so the ease with which crazing occurs depends on the manufacturing process as well as the stresses experienced by the cover. The stress levels at which crazing is initiated can be considerably reduced by the presence of organic solvents.

Crazes contain some polymer material and are therefore still able to withstand some stress. After a continual cycling of stress, however, the crazing may develop into cracks that extend right through the material, and thus bring about fatigue failure of the cover. The vulnerability of plastics to fatigue fracture can be reduced by the absorption of water.

Fibre separation and delamination are two ways in which composite materials can disintegrate following a differential thermal expansion of the constituents. In laminated plastics the durability of the adhesive is clearly of importance.

The majority of plastic covers show some signs of material degradation during service [2] - [6]. Discoloration and crazing are most often observed, although softening and warping are also common.

2.1.5 Degradation of plastic cover materials

The degradation processes that take place in plastic materials are complex physical and chemical reactions, influenced in different ways by a number of interacting environmental variables, including temperature, ultraviolet radiation, moisture and atmospheric pollutants.

The following brief introduction to these mechanisms is based largely on two sources: an article by H Wennerholm of the National Testing Laboratory in Sweden [7], and the monograph on polymer degradation by W Schnabel [8].

The molecular changes that may accompany degradation can be classified as:

- scission of main chains
- chemical modification of main chains
- transverse bonding between main-chain units

The scission ('rupture', 'breakage' or 'lesion') of main-chain molecules causes a reduction in the average molecular weight of the material, and generally results in softening. Conversely, transverse bonding (or 'cross-linking') between the main chains results in hardening and embrittlement. A high degree of transverse bonding can result in cyclization - the formation of endless molecular structures characteristic of gels.

Among the principal physical causes of bond rupture leading to degradation in plastic covers are photochemical reactions, oxidation, and hydrolysis. Temperature has a strong influence on degradation. It can directly initiate degradation in polymers having a low softening point, and the reaction rates of the other degradation processes generally increase exponentially with temperature.

Photochemical processes are initiated by the absorption of solar radiation. The bonding energy of a polymer chain is typically in the region of 210 - 420 kJ mol^{-1}, and the energy per mole of light (taking the photon as elementary unit) can be calculated as the product of Avogadro's number, Planck's constant and the speed of light, divided by the wavelength (λ) of the light - giving a value of about (120 μm/λ) kJ mol^{-1}. Hence polymers are most susceptible to radiation of wavelength in the range 285 - 570 nm. The near-ultraviolet part of solar radiation (295 - 400 nm) is the most important for polymer degradation, since radiation of wavelength less than 295 nm is almost completely absorbed by the atmosphere.

Some cover materials, such as PMMA and PTFE, are transparent to ultraviolet radiation, and are therefore stable to photochemical degradation. Others can be stabilized with suitable additives.

The normal mechanism for oxidation degradation in commercial polymers is auto-oxidation. The process of auto-oxidation is a chain reaction initiated by thermal or photochemical reactions, in which free radicals produced by the rupture of bonds react with oxygen diffusing into the polymer. Depending on the initiation mechanism, this can be followed by a crystallization of the broken chains and an increase in density, or by branching and transverse bonding between main chain units and the onset of brittleness. The rate of auto-oxidation is limited by the diffusion rate of oxygen in the polymer, which is reduced by crystallization but increased by branching or transverse bonding.

Oxidation degradation causes discoloration as well as a rapid deterioration of mechanical strength.

Hydrolysis is a chemical reaction with water which again tends to cause a deterioration of strength due to chain rupture. The cover materials most susceptible to degradation by hydrolysis are polyesters and PVC.

Studies of the hydration of PET have shown that the density increases with the degree of hydrolysis, but that the diffusion rate of water is not the principal factor limiting hydrolysis. In general, it is found that the mechanism and rate of hydrolysis in alkaline media differ from those in neutral or acidic media.

Microbiological degradation of polymers generally takes place by enzymatic attack, and hence there is a tendency for the polymers most susceptibility to hydrolytic degradation to also be the most readily biodegradable.

The processes associated with outgassing from polymeric materials are described by Luck and Mendelsohn [9] [10]. In the first stage of outgassing, volatile organic compounds diffuse out of the polymer at elevated temperatures. The non-condensable components are relatively harmless and gradually seep out of the collector, while the condensable volatiles condense on the inside of the glazing and other cool areas. The condensate may itself be a clear liquid which evaporates cleanly, but it may leach ions out of the glazing which are left as an opaque residue ("chalking"). Alternatively, thermal-, oxidation-, or ultraviolet-induced reactions may convert the condensate into a solid, non-volatile polymer which, after repeated cycles of condensation and evaporation, accumulates to form a surface coating that can seriously reduce the optical transmittance of the cover.

2.2 Sealing materials

2.2.1 Materials used for collector sealing

A wide range of synthetic rubbers, thermoplastic elastomers and resins are used as sealants for solar collectors. The properties of these polymers generally depend on the ratio of the constituents and on the manufacturing or vulcanization process. Accordingly, they may take the form either of preformed gaskets or of sealing caulks. Among the materials used are:

- natural rubber (polyisoprene)
- silicone (polysiloxanes) - 'Silastic'
- neoprene (polychloroprenes)
- butyl rubber (isobutylene-isoprene copolymers)
- (poly)acrylic rubber (polyacrylates)
- polysulphide elastomers - 'Thiokol'
- chlorosulphonated polyethylenes - 'Hypalon'
- epichlorohydrin elastomers - 'Hydrin'

- fluorocarbon elastomers - 'fluoroelastomers' 'Viton'
- (poly)urethane rubbers, thermoplastic elastomers and resins - 'Adiprene' 'Estane'
- rubbers formed from copolymers of ethylene and propylene monomers (EPM) - 'ethylene-propylene rubber (EPR)' 'Nordel' - and from terpolymers of ethylene, propylene and diene monomers (EPDM)

2.2.2 Failure modes of gaskets and sealants

The degradation mechanisms in sealing materials are similar to those of polymeric cover materials, except that caulks are generally more susceptible to outgassing. It may also be noted that poly(methyl siloxane) is transparent to ultraviolet radiation, and hence stable to photochemical degradation, while the polyurethanes are generally more susceptible to hydration and microbial attack.

Inspection of installations has shown that softening, powdering, embrittlement, shrinkage and contamination are all common forms of degradation of sealing materials.

2.3 Insulation materials

2.3.1 Materials used for collector insulation

The materials used as insulation in solar collectors include minerals, such as:

- glass fibre (including glass wool)
- mineral wool* (including rock wool)
- glass foam

and expanded foams of:

- polystyrene
- phenol formaldehyde
- urea formaldehyde
- (poly)urethanes
- polyisocyanurate**

*(Note: The term "mineral wool" is often used to include glass fibre.)

**(Note: While polyisocyanurate is chemically a polyurethane, it is physically very different from the materials normally referred to as "polyurethanes".)

The properties of the foams generally depend on the manufacturing process - whether they are carbon-dioxide blown or halocarbon blown, for instance.

2.3.2 Failure modes of collector insulation materials

The failure modes of plastic foams used for collector insulation are broadly the same as for polymeric glazing materials. The type and severity of the degradation mechanisms observed reflect the excess temperatures of collector interiors above ambient, especially when there are one or more layers of glazing. They include:

- discoloration
- warping
- shrinkage
- cracking
- corrosion
- loss of thermal insulation

The discoloration is commonly a browning coloration resembling scorching. Warping is usually a bulging caused by expansion. Cracking may follow a process of embrittlement. In foams, corrosion tends to result in a complete breakdown of the material, and the result is described as "powdering".

Loss of thermal insulation in expanded foams may be caused by the outward diffusion of the gas used in expanding the foam.

The chemical processes which accompany degradation in polymeric insulation materials are equivalent to those in the cover materials and have the same basic causes. It may again be noted that the polyurethanes are generally more susceptible to hydrolysis and biodegradation.

Insulation materials may also suffer from waterlogging (saturation by water). Unlike hydrolysis, however, which is a chemical reaction with water, waterlogging is not of itself a form of material degradation.

In the CEC survey [6] 16% of installations showed discoloration, powdering or loosening of the insulation. Saturation by water was found in 6%.

2.4 Absorber materials

2.4.1 Materials used in collector absorbers

Generally the absorber of a collector has a number of distinct elements, which may be of quite different materials. The absorber plate is commonly made of metals such as:

- aluminium (alloy)
- copper
- (mild, stainless or enamelled) steel

or of polymeric materials such as:

- high-density polyethylene (HDPE)
- polypropylene = poly(methyl ethylene) (PP)
- ethylene-propylene terpolymers (EPDM)
- poly(vinyl chloride) (PVC)
- polycarbonate (PC)
- butyrate (CAB)

The plate may itself form the heat-transfer fluid duct or it may contain bonded header and riser tubes, most commonly made of copper for compatability with the piping of the heating system.

In some flat-plate collectors the absorber plate is transparent (PC or CAB, for example), and a black heat-transfer fluid is used to absorb the solar radiation directly. Usually, however, the absorber plate has an absorbing coating, which is formed on a substrate consisting either of the plate itself or of a layer of another material bonded to the plate. Materials used for absorber surfaces (with suitable substrates) include [6]:

- selective or matt-black paints, including enamel, alkyd, acrylic and siliconized-polyester paints (sprayed directly onto most absorber plates)
- tin oxide (sprayed onto enamelled-steel substrate)
- black chrome (electrodeposition onto copper, aluminium and mild- or stainless-steel substrates)
- black cobalt (electrodeposition onto mild steel)
- black nickel (electrodeposition onto copper and mild steel substrates, or electrochemical conversion of nickel-foil substrate)
- (black) copper oxide (electrochemical conversion of copper substrate)
- anodized aluminium (electrochemical conversion of aluminium substrate)
- blue stainless steel (electrochemical conversion of stainless-steel substrate)

2.4.2 Failure modes of collector absorbers

The forms of material failure observed in collector absorbers include

for absorber substrates and coatings:

- corrosion
- detachment

and for absorber plates and solders:

- corrosion
- warping

Corrosion of absorber coatings takes place under the combined influence of moisture, high temperatures and atmospheric gases, including pollutants. Were it not for the stresses of high temperatures, particularly in glazed collectors, and for temperature cycling, the absorber coatings would not be particularly susceptible to degradation. Indeed, it is interesting to note that many absorber coatings have traditionally been used as protective or decorative finishes for metal surfaces.

Frequently the absorber plate may be soiled by materials such as dirt, salt or soot, which enter the collector through the ventilation holes or through leakage points, and which can contribute to the corrosion processes. Condensation dripping from the glazing bars of the cover may also carry corrosive materials that have been leached out of the covers. The effect of the corrosion may or may not be to degrade the optical properties of the coating. One form of corrosion that does change the absorption is known from its appearance as 'white rust'.

The detachment of absorber coatings or substrates may be the result of a differential expansion between the bonded materials or of a degradation of an adhesive.

Metal absorber plates and solders (the same applies to piping) may be subject to two independent corrosive attacks: external corrosion due to the atmosphere, or internal corrosion due to the heat transfer fluid. In each case, depending on the mechanisms responsible, the corrosion may be of several different forms:

- pitting corrosion
- stress corrosion
- galvanic corrosion
- biological corrosion

Pitting corrosion is highly localized on the metal surface, and is nucleated by flaws in a protective coating or in the metal or by particles of dirt or chemical pollutants.

Stress corrosion is seen in regions of stress in the metal, most commonly around rivets and bolts, where the susceptibility to the other mechanisms of corrosion is enhanced. Repeated thermally-induced stress cycling of metals leads eventually to cracking of the metal through fatigue failure.

Electrolytic (or 'galvanic') corrosion is an electrochemical process associated with the flow of an electrical current between two metals (or two areas of the same metal) through an electrolytic solution. The rusting of iron and steel is a common example. The rate of corrosion is influenced by the acidity of the solution, the presence of oxidizing agents in the solution, the products of corrosion, and the thermal regime. The products of corrosion may accelerate or retard further corrosion according to their chemical and physical character: they may for example form a protective film on the metal surface. The wide range of fluids used in solar collectors includes air, water (with or without corrosion and freezing inhibitors), oil, and refrigerants, and each of these fluids has its own corrosive properties.

Excess temperatures generally increase the corrosion rates appreciably. A study by Keller and Bruck [11] of electrolytic corrosion in the fluid conduits of solar collector loops showed that higher heat-transfer-fluid flowrates also increase the rate of corrosion. This could be attributed to the abrasive action of suspended solids and to an increase in the rate of removal of corrosion products.

Biological corrosion results from the metabolic activity of microorganisms such as bacteria, algae and fungi.

In the CEC survey [6], about one in three of the installations had corrosion, and in about a third of these cases it was thought to be severe. Pitting and powdering of aluminium, rusting of steel, and galvanic corrosion between risers and fins of differing material were observed, and internal corrosion was inferred from the colour of the heat transfer fluid. Detachment of the surface coatings was seen in about 15% of installations, but it was generally thought to be due to inadequate preparation of the substrate rather than to a degradation of the material. Buckling of the absorber due to thermal stresses or to stresses during the manufacture were seen in 10% of the inspected installations.

2.5 Casing and fixing materials

2.5.1 Materials used for collector casings and fixings

The many materials used to form collector enclosures and supporting brackets include metals:

- aluminium alloys
- (galvanized or nickel-plated) mild steel
- stainless steel

plastics:

- GRP
- PVF

and wood, either as

- plywood

or

- timber (lumber)

In addition, the following materials have been used for flashings:

- zinc
- lead
- reinforced bitumen felt

2.5.2 Failure modes of collector casings and fittings

The failure modes of metal and polymeric casing and fixing materials are exactly as described for cover and absorber materials. The degradation of wood in collectors (or in roofing timbers in proximity with roof-integrated collectors) is generally the same as for timber in conventional buildings, except that the conditions may be somewhat different. The unusually high temperatures around collectors, for example, have been seen to result in an abnormally high rate of exudation of resin from roofing timbers. And rotting of timbers may result from leakage around flashings.

In the CEC survey [6], corrosion of mounting brackets and supporting frames was found in in 29% of systems. Often it was clearly the result of damage to protective coatings caused by rough handling or bolt tightening, or due to the use of dissimilar metals.

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3 QUANTIFICATION AND MEASUREMENT OF DEGRADATION

Field inspection remains a valuable method of assessing degradation. It is relatively quick and easy, and reporting formats exist [1] [2] to ensure that the inspection is complete and systematic. Much has been learned from visual inspection of solar installations about the types of degradation to which collector materials are susceptible, how frequently they occur, and how serious are their consequences.

A long-term objective of collector durability studies is to be able to predict the rates of degradation of collector materials in given environmental and operational conditions. This would make it possible to estimate and hence to optimize collector lifetimes. To achieve this it is necessary to concentrate on methods of quantifying and measuring the different forms of material degradation.

The methods of measuring degradation suggested in the following sections are as far as possible standard methods, for which full and validated procedures are available. Some are already commonly used in solar-collector durability studies; others have had a very limited use because, for example, they need expensive dedicated equipment or special expertise. Some of the methods are suggested tentatively, because they may prove to be useful for measuring collector degradation but so far there has been no experience in using them among Task III participants.

3.1 Optical properties

The participants of Task III are presently compiling a handbook of recommended practices for the measurement of optical properties of collector components [3]. In view of this, the purpose of the present section is confined to indicating the use of optical measurements in the detection and quantification of material degradation. Details of the laboratory techniques employed will be found in the handbook.

3.1.1 Solar transmittance of cover materials

Two basic approaches are for the measurement of the optical transmittance of collector cover materials: spectral measurements using an integrating-sphere spectrophotometer, and total measurements using the sun or a solar-simulator lamp and a pyranometer or other detector.

A standard method for spectrophotometer measurements is provided by the ASTM Standard E 903-82 [4], which updates Method A of ASTM Standard E 424-1971 [5]. The new standard improves the integration-sphere techniques and provides an absolute measurement.

Measuring the optical properties of corrugated and diffusive materials is generally difficult because of the problems of illuminating a sufficiently large sample of the material and collecting all the transmitted radiation. Zerlaut and Anderson [6] of DSET Laboratories Inc. have published details of an integrating sphere of diameter 2.44 m constructed from a commercial polyester fibreglass water tank coated internally with a purpose-made barium sulphate paint. The light source for the integrating sphere is the sun, with an automatic-tracking siderostat designed to concentrate the solar radiation and direct it through a window into the entrance port of the integrating sphere.

(The near-noon desert sun gives a good approximation to the ASTM Standard 1.5 Air Mass spectrum [7] for most materials.) The detector is a high-sensitivity thermopile, mounted in an Eppley Model 8-48 pyranometer housing, and fixed on the inside surface of the sphere at a position where it receives no direct radiation from the source.

The transmittance of samples of 305 mm diameter can be measured using this equipment. For global measurements the sample is placed across the entrance port. The angle of incidence can then be varied from 0 to 60° by moving the whole sphere relative to the incident beam. For spectral measurements the sample is placed in an occluding tube and rotated relative to both the incident beam and the sphere. A measurement accuracy of 0.5% is obtained.

For total measurements of transmittance, Method B of ASTM Standard E 424 [5] and a similar method in ASHRAE Standard 74-1973 [8] provide standard techniques. Because of the expense of spectrophotometer facilities, methods of this type are likely to be much more commonly used for durability studies.

3.1.2 Haze in cover materials

The erosion of covers by abrasion or corrosion generally causes the surface to diffuse light passing through it. The same effect may be produced by chemical or physical changes within the the material. The property is called 'haze', and is defined as the percentage of normally-incident radiation that is scattered by more than 2.5° by forward scattering on passing through the material. It is measured with a 'hazemeter'.

Standard instruments and procedures for measuring haze are provided by ASTM Standard D 1003 [9] and BS2782:1970:method 515A [10].

3.1.3 Yellowing of plastic cover materials

The yellowing of plastic materials as a result of weathering can be measured as a change in "yellowness index". A definition of yellowness index and specifications for the apparatus and procedures to measure it are set out in ASTM Standard D 1925 [11]. Reference is also given to commercial instruments that provide a direct reading of the yellowness index in accordance with the standard.

3.1.4 Solar absorptance of absorber coatings

The solar absorptance of absorber coating materials is normally obtained indirectly from measurements of the solar reflectance. (For opaque materials the sum of the absorptance and the reflectance at any wavelength is 1.) The directional(incidence)-hemispherical(reflection) solar reflectance can be obtained as a function of incidence angle either from spectral measurements using an integrating-sphere spectrophotometer or from total measurements made with the sun or a simulator lamp as source and a pyranometer or other detector in an integrating sphere.

The recommendations for spectrophotometer measurements provided by ASTM Standard E 903 [4] are updated from those in ASTM Standard E 424 [5], while ASTM Standard E 892 [7] gives a standard 1.5 air mass spectrum that can be used for weighting the spectral measurements to obtain an appropriate solar value. A procedure for total reflectance measurements is given in ASHRAE Standard 74-1973 [8].

Zerlaut and Anderson [6] give details of the use of their 2.44 m diameter integrating sphere for absorptance measurements. In the reflectance mode of operation, the sample is placed in the centre of the integrating sphere at an arbitrary angle relative to the incident beam but oriented so that no radiation is directly reflected from the sample to the pyranometer.

A very useful overview of methods of measuring the radiative properties of surfaces is given in the report by Dorman [12].

3.1.5 Thermal emittance of absorber coatings

Indirect spectral measurements of directional-hemispherical thermal emittance can be made with an integrating-sphere infrared spectrometer. However, since instruments with a sufficiently wide infrared bandwidth are not commonly available, direct total measurements with simple portable emissometers may be much more widely used for durability studies. Commercial emissometers are available, and details of one model can be found in the report by Dorman [12].

Other methods of measuring thermal emittance include calorimetric methods and direct comparison with a black body. Further details can be found in [2] and [12]. A standard calorimetric method is specified in ASTM Standard E 434 [13].

Waksman and Roberts [14], reporting on studies done at the National US Bureau of Standards, concluded that spectral measurements of infrared reflectance were a more sensitive indicator of structural changes in the absorber than measurements of the total normal emittance according to ASTM Standard E 408 [15], which were in turn more sensitive than solar-reflectance measurements according to ASTM Standard E 424 [5].

3.2 Mechanical properties

3.2.1 Plastic materials

There are a number of measures of the strength of plastic materials that may may be of use in quantifying mechanical degradation, and for which national and international test methods have generally been established. These include:

- tensile strength
- flexural strength
- compressive strength
- shear strength
- impact strength
- tear strength
- indentation strength
- bond strength

Each strength parameter is a measure of the ability of the material to withstand a particular form of applied force. They are generally measured on specially formed samples of the material, and would therefore be measured in exposure trials of individual materials rather than monitored in integrated collector modules.

The tensile strength measures the resistance of a suitably-formed sample to failure under tension. It is necessary to make a distinction here between ductile materials, in which fracture follows the onset of plasticity (at the 'yield point'), and brittle materials, in which fracture is not preceded by yield. In brittle materials the tensile strength is measured by the maximum stress in brittle fracture (the 'brittle strength'), while in ductile materials both the yield stress, which measures the resistance of the material to plastic deformation, and the stress at break point, which measures the resistance to fracture, provide a useful measure of tensile strength.

It should be noted that brittle or ductile behaviour is not an inherent property of a material but is affected both by temperature and the speed of application of the stress. At temperatures close to the glass-transition temperature plastic materials usually exhibit ductile behaviour with a low yield stress. As the temperature is lowered the yield stress increases until, at a critical temperature known as the 'brittle point', the yield stress becomes equal to the fracture stress and the material begins to show brittle behaviour. Increasing the speed of application of the stress generally increases the yield strength faster than it decreases the fracture stress, and thus moves the brittle point to higher temperatures [16].

Methods for measuring the tensile strength of plastics may be found in ASTM Standard D 2990 [17] and BS2782:Methods 301K, 320A-F [10].

The flexural strength (cross-breaking strength) of a material measures its ability to withstand bending forces. It is usually measured on a rectangular sample, which is placed on two supports and loaded in the middle. National and international standard test procedures for flexural strength are specified in ASTM Standard D 790M [18], BS2782:Methods 304A-E [10], and ISO 178 [19].

The brittle strength in flexure is usually higher than that in tension by a factor of about 1.5 (the 'rupture factor'). The main reason for this is that crazes and cracks grow less readily in the direction of flexural stress. Brittle fractures that originate at the machined edges of the sample rather than on the moulded surfaces are easier to identify and discount in flexural tests, so the brittle strength in flexure of the bulk material can be more reliably determined than the brittle strength in tension [16].

The compressive strength, or 'crushing strength', may be a useful parameter with which to measure the structural breakdown of foam insulation. A standard test procedure for the measurement of compressive strength is given in BS2782:Method 345A [10].

The shear strength of plastic sheet material is measured by the punching a hole in a sample using a specially designed apparatus. BS2782:Methods 305A,B [10] and ASTM Standard D 732 [20] specify suitable forms of apparatus and test procedures.

The impact strength ('impact resistance') of a material measures its resistance to breakage under an impulsive force, as might be caused by a sharp blow or by being dropped. The speed of impact implies that the fracture will be brittle, and because fractures normally initiate at a flaw or other stress point, the test sample is notched to provide such a point. Many test standards exist for measuring the impact strength of plastic materials, including ASTM Standard D 256 [21], ASTM Standard D 1822 [22], BS2782:Methods 306A-E,352D [10], ISO 180 [23], and ISO 179 [24]. A critical review of these methods is given by Vincent [16].

Tear strength is measured for thin flexible sheet materials, and may be of use as a measure of the strength of the materials employed for inner glazings. Standard test methods may be found in BS2782:Methods 308B,360B [10].

Indentation tests measure the hardness or softness of materials by their resistance to strong localized compression. For glazing materials a method using a pointed indentor is likely to be suitable, while for insulation and sealing materials there are methods in which the indentation is made with a steel ball-bearing.

Very many measures of indentation hardness or softness exist: BS2782:Method 365A [10] measures a 'softness number'; other parameters include the Brinell, Vickers, Knoop, Rockwell, Barcol, and Shore durometer hardness numbers. Methods of measuring these parameters are reviewed by Crawford [25]. A standard method for measuring the Rockwell hardness number of plastics is given in ASTM Standard D 785 [26], while for measuring the durometer hardness of gasket and sealing materials the techniques of ASTM Standard D 2240 [27] may be useful.

The bond strength is a measure of the force needed to separate the layers of a laminated material (the 'adhesion strength') or the fibres or other fillers from a reinforced plastic (the 'cohesion strength'). A test for the bond strength of plastics is specified in ASTM Standard D 952 [28], and a series of adhesion tests for PVC sheet is specified in BS2782:Methods 310A-C,E-F [10].

3.2.2 Metals

Since corrosion is by far the most significant form of metal degradation in solar collectors, and since corrosion does not usually occur uniformly on a material, only non-local mechanical properties of metals, such as tensile strength and impact strength, are likely to be of interest for collector degradation studies. The tensile strength of metallic materials can be tested according to ASTM Standard E 8 [29], and the impact strength according to ASTM Standard E 23 [30].

The integrity of welded seams in absorber plates is usually checked by pressure testing during manufacture. To study the deterioration of seams as a result of corrosion it would be necessary to have laboratory tests for the bond strength of the weld or its tightness against leakage.

3.2.3 Absorber coatings

Standard methods which can be used for testing the integrity of absorber coatings include ISO 2409 [31] and ISO 4624 [32] to measure the adhesion between the coating and the substrate, and ISO 4628 [33] to assess the degree of blistering, rusting, cracking or flaking.

An example of an automatic device for testing the cohesion of hard and brittle coatings and their adhesion to softer but tougher substrates has been developed by the Laboratoire Suisse de Recherches Horlogeres. A smoothly rounded diamond point with a constant or gradually increasing load applied to it is drawn over the surface. The acoustic emission produced by the point depends on the nature of the damage to the surface, and thus a chart recording from a piezoelectric transducer is used to give qualitative and quantitative information about the mechanical strength of the coating.

3.3 Corrosion rates

3.3.1 Loss in weight

The principal method of quantifying the corrosion of metals is by measuring the loss of metallic mass. This can normally be done only on small samples of metal. For an accurate measurement it is important that the sample is thoroughly cleaned before being reweighed, using some mechanical, chemical or electrochemical method which will remove all the corrosion products while leaving as much as possible of the uncorroded metal.

A standard practice for preparing, cleaning, and evaluating corrosion test specimens may be found in ASTM Standard G 1 [34].

3.3.2 Pitting

When pitting corrosion has occurred, the degree of corrosion may be measured by observing the shape, size and distribution of the pits. The pit depths can be measured using a calibrated microscope or (if they are sufficiently large) by means of a needle-pointed depth gauge.

Recommended procedures for examining and evaluating pitting corrosion are set out in ASTM Standard G 46 [35].

3.3.3 Mechanical properties

Corrosion usually results in a change in the mechanical properties of the material, such as softening or embrittlement. Hence changes in mechanical properties may also been used as a measure of the extent of the corrosion. Suitable tests were suggested in paragraph 3.2.2 above.

3.3.4 Chemical changes in the heat-transfer fluid

As part of a corrosion surveillance program on a large solar heating plant at the Swiss Federal Institute for Reactor Research [36], an investigation was conducted into whether the progress of corrosion in the circuit could be determined from analysis of the heat-transfer fluid. Monitoring the pH, electrical conductivity, ethylene-glycol concentration, inhibitor and dissolved metals in the fluid over a period of 35 months showed that the concentration of metals in the fluid fluctuated seasonally with the amount of circulation, apparently as the result of the settlement and recirculation of corrosion products. It was concluded that chemical analysis of the fluid gives no reliable indication of the amount and progress of corrosion.

3.4 Outgassing products

A laboratory measurement of outgassing from a polymeric caulk, sealant, insulation material, coating, or sheet material is obtained by heating a sample in the presence of a cooled plate to collect the condensable volatile products. The mass loss of the sample gives the total mass of outgassing products, the increase in mass of the plate gives the mass of the condensate, and the difference is taken to be the mass of the non-condensable products.

In the test apparatus described by Luck and Mendelsohn [37] [38], the cooled plate is a sodium chloride crystal which can be placed directly into an infrared spectrometer in order to to identify the chemical species present in the condensate. Details of the apparatus and procedure are given in the papers.

The effect of outgassing on cover materials may be measured directly as a deterioration in the optical properties.

3.5 Collector thermal performance

The insensitivity of collector thermal performance to most forms of degradation in collector materials together with the uncertainties associated with the measurement of thermal performance make this a rather poor measure of collector degradation [39] [40] [41]. Nevertheless, collector thermal performance is often used as a test for a significant degradation of optical properties.

3.5.1 "Zero-loss efficiency"

The intercept on the efficiency axis of a collector steady-state thermal performance characteristic represents the collector efficiency when the mean fluid temperature in the collector is at the collector ambient temperature, i.e. when there is no net thermal exchange between the fluid in the collector and the ambient air. It is commonly referred to as the "zero-loss efficiency" (although this term is now thought to be misleading), and it is denoted by η_o.

From the standard Hottel-Whillier-Bliss theory of the flat-plate collector [42] the efficiency intercept can be expressed as

$$\eta_o = F'(\tau\alpha)_{e,n} , \tag{3.1}$$

where F' is the collector efficiency factor and $(\tau\alpha)_{e,n}$ the effective transmittance-absorptance product. The measurement of η_o typically has an absolute accuracy of about 5%, and can thus be used only to detect changes in the effective normal transmittance-absorptance product significantly in excess of 5%.

3.5.2 Heat-loss coefficient

The slope of a collector thermal performance characteristic is known as the collector heat-loss coefficient, and denoted by U. U can be expressed as

$$U = F'U_L , \tag{3.2}$$

where U_L is the overall heat-loss coefficient of the collector.

Since U can normally be measured to an accuracy of no more than about 0.5 W m^{-2}, its measurement can be used only to detect degradation resulting in changes to the overall heat-loss coefficient of this order of magnitude.

3.6 Stagnation temperature

The use of the difference between the collector absorber temperature in stagnation and the ambient temperature as an indicator of degradation of optical properties has certain advantages compared with thermal efficiency measurements, including the simplicity of the apparatus and the accuracy obtainable with simple temperature probes [43]. Waksman and Thomas [44] concluded that the absorber stagnation temperature methods evaluated during the NBS test programme were at least as good an indicator of performance (except for changes in the bond conductance) as a standard thermal performance test. The method has been used in Switzerland [41]. In the Netherlands [45] a simulation study of the effects of changes in the optical properties was funded by the CEC for its Collector and System Testing Group.

The main disadvantage of this approach is the high sensitivity of the stagnation temperature to ambient conditions, especially to the air speed and to departures from steady-state. Dawson, Thomas and Waksman [46] found that the effects of transients could be eliminated by the use of daily-integrated temperatures (as proposed by Birnbreier [47]) in place of steady-state values. Nevertheless, the method requires clear-day conditions (at least 20 MJ m^{-2} day^{-1}) and closely-matched test conditions in order to detect changes of the order of 0.1 in the solar transmittance, absorptance or emittance.

A thorough appraisal of the method and details of suitable measurement techniques can be found in the the papers by Thomas, Dawson and Waksman [43] [46].

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4 METHODS OF MEASURING INTERNAL ENVIRONMENTAL VARIABLES

The principal environmental factors influencing material degradation in solar collectors were identified in the previous chapter as humidity, moisture, temperature, atmospheric pollutants and ultraviolet radiation. In the present chapter practical methods are outlined by which these variables can be measured both inside and outside the collector.

The factors discussed here are all primary factors of degradation; taken together they are sufficient to characterize the corrosive environment of the collector materials. Their values will depend on the mode of operation of the collector, and they will be influenced by other factors such as ventilation rates and water-penetration rates. It is intended to treat these secondary factors - and their dependence in turn on the speed and direction of the wind and on the rate of precipitation - in the report being prepared on collector qualification tests.

4.1 Humidity

4.1.1 Methods of quantifying humidity

If a volume V of moist air contains a mass m_w of water vapour mixed with a mass m_a of dry air, then

- the absolute humidity (d) of the air is defined as the mass of water vapour per unit volume (of moist air):

$$d = m_w/V \, , \tag{4.1}$$

- the (mass) mixing ratio (r) is the ratio of the mass of water vapour to the mass of dry air:

$$r = m_w/m_a \, , \tag{4.2}$$

- the specific humidity (q) of the air is the ratio of the mass of water vapour to the total mass (of moist air)*:

$$q = m_w/(m_w+m_a) = r/(1+r) \, , \tag{4.3}$$

- the relative humidity (U) is the ratio of the mass of water vapour to the mass of water vapour that would saturate the same volume of air at the same temperature (m''_w):

$$U = m_w/m''_w \, . \tag{4.4}$$

Relative humidity is usually expressed as a percentage.

*(Note: The specific humidity was formerly defined as the quantity now referred to only as the 'mixing ratio'. The definition given here follows SI convention. In practice the terms are interchangeable, however, since under normal atmospheric conditions the mixing ratio and the specific humidity are very nearly equal.)

At normal atmospheric pressures and temperatures the moist air behaves closely like a mixture of perfect gases. If the total pressure is p and the partial pressure of the water vapour is e when the thermodynamic temperature is T, then it follows from the equation of state for an ideal gas that

(4.5) $$eV = m_w RT/M_w$$

and

(4.6) $$(p-e)V = m_a RT/M_a \ ,$$

where R is the universal gas constant (8.31441 kJ $\text{kmol}^{-1}\ \text{K}^{-1}$), M_w the molecular weight of water (18.015 kg/kmol) and M_a the molecular weight of dry air (28.96 kg/kmol). Also, if e"(T) is the saturation vapour pressure at temperature T, then

(4.7) $$e''(T)V = m''_w RT/M_w \ .$$

Hence, an alternative expression for the absolute humidity is

(4.8) $$d = eM_w/RT \ ,$$

while the mixing ratio can be calculated from

(4.9) $$r = M_w e/M_a(p-e) = 0.622e/(p-e) \ ,$$

and the relative humidity from

(4.10) $$U = e/e''(T) \ .$$

Methods of measuring the absolute humidity of air involve passing air at a constant flowrate through a cell where the water undergoes a chemical or electrochemical interaction. In one method the air is passed over a solid absorber and the heat of absorption or desorption of the water is measured, and in another the air passes between thin films of phosphoric acid on platinum electrodes and the current from the dissociation of the water is measured. Such methods are sensitive and accurate but somewhat cumbersome.

Instruments for measuring relative humidity are usually based on the measurement of the change in mechanical or electrical properties with hydration. For scientific purposes the electrical types are most suitable; they are usually constructed of two wires wound onto an insulating core and separated by a hygroscopic material whose electrical resistance or capacitance is proportional to the amount of water absorbed.

Measurements of relative humidity are generally less sensitive and less accurate than measurements of absolute humidity, but are convenient and sufficiently accurate for collector degradation studies. Moreover, hydrolysis and corrosion are generally governed by the relative humidity of the air rather than the absolute humidity.

Another approach to the measurement of humidity is by way of the dew point (T_d), defined to be the temperature to which the moist air would have to be cooled at constant pressure before it became saturated. Since, from (4.5) and (4.6),

(4.11) $$pV = (m_w/M_w + m_a/M_a)RT \ ,$$

then if p is constant during cooling, so is RT/V. In that case (4.5) shows that e is also constant. It follows that the water vapour pressure before cooling is equal to the saturation vapour pressure at the dew point:

(4.12) $$e = e''(T_d) .$$

The air temperature is easily measured, and the dew point is found by cooling a mirrored surface until dew forms on it. Tables of saturation vapour pressure versus temperature are available, and hence the absolute humidity can be found as

(4.13) $$d = e''(T_d)M_w/RT ,$$

and the relative humidity as

(4.14) $$U = e''(T_d)/e''(T) .$$

Commercial instruments are available which can measure the dew point automatically. The variation of saturation vapour pressure with temperature is stored in the memory of the instrument, and the value of the relative humidity is indicated directly.

4.1.2 Instruments suitable for measuring the humidity inside solar collectors

The humidity will vary over the inside of a collector depending on the temperature gradients from the casing to the interior and from the covers to the absorber plate, and as a result of forced ventilation and convection. This can be directly observed by the pattern of condensation on the collector surfaces. Ideally, therefore, an array of sensors would be required to properly monitor the humidity within a collector. It may be that in practice only a single humidity detector can be used, with its positioning limited by the need to introduce it into the collector through ventilation holes or holes made to accommodate other probes. Consistent with these requirements the best position for the sensor might be where the greatest humidity is likely to occur.

Since the value of the humidity is very sensitive to temperature, it is important that any temperature associated with the humidity measurement should be made with the thermometer in close thermal contact with the humidity sensor. For this reason an instrument which combines humidity and temperature sensors is likely to be most useful. For the results to be valid it is equally important that the sensors have a small thermal mass and radiative properties similar to those of the collector interior.

Commercial humidity and temperature probes are severely limited as instruments for monitoring the inside of solar collectors. The main problem is that condensation on the protective filter surrounding the sensor may take some hours to evaporate after the temperature has risen above the dew point. In the meantime, readings of 100% relative humidity are given irrespective of the actual value in the collector, and the temperature sensor gives a depressed (wet-bulb) reading. The instruments are intended either to be well ventilated or to operate only within a limited range of humidity, and neither of these conditions usually applies to the interior of solar collectors. Also, because of corrosion, the lifetime of the sensors may be limited to as little as three months.

Another means of determining the humidity inside a collector is to draw off samples of air from the collector for external measurement. The value obtained would be an average, and one difficulty with this approach is that the sampling may have a significant influence on the ventilation of the collector.

In principle it should also be possible to measure the dew point within the collector but the Task Participants are not aware of an instrument which is sufficiently small for this purpose.

4.2 Moisture

4.2.1 Instruments for measuring moisture

Surface moisture is not such a well-defined physical quantity as humidity, but there are detectors which sense the presence of liquid water and give some measure of the amount of water present. For corrosion studies various attempts have been made to define "time-of-wetness" parameters that would quantify the degree of exposure to wet, corrosive conditions. The problem, however, is how to describe what is an essentially complex physical process by means of a single parameter.

A proposal for a standard measurement of surface time-of-wetness based on a commercial instrument (the Epitek "Sereda" Miniature Moisture Sensor, Model SMMS-01) has been drafted by the ASTM Committee G01-04 on atmospheric corrosion [1]. The sensor is a passive instrument containing an electrochemical cell with alternate electrodes of copper and gold on an insulating substrate. In contact with water or ice, it generates a 20 to 40 mV DC voltage across a 10 megohm load. The sensor has a low thermal mass to accurately reflect the conditions of the surface to which it is attached, and its manufacturers claim that in most environments it can be left in place for some years. Experience has shown [2] that this kind of moisture sensor is very suitable for monitoring condensation within solar collectors.

4.3 Temperature

4.3.1 Upper absorber-plate surface

A method commonly used for measurements of the surface temperature of the collector absorber is to attach small platinum-resistance thermometers to the surface using a heat-conducting adhesive. An alternative idea is to mount small infrared detectors inside the glazing, facing the absorber. It is important that the sensors do not absorb solar radiation themselves, and this can be avoided by covering them with a reflecting patch and by calculating appropriate correction factors.

The absorber-plate temperature of unglazed collectors can be monitored using infrared cameras.

4.3.2 Lower surface of absorber plate

A method which has been used to measure the lower-surface temperature of a collector absorber without dismantling the collector is to insert a spring-loaded thermocouple probe through a hole in the back of the collector casing [3]. The design of this probe is such that the same instrument can be used for collectors with different materials and thickness of insulation. It is mounted on the collector by drilling a 10 mm diameter hole in the back of the cover and using a gasket cutter to remove a core of the insulation. The probe, with a heat-transfer compound on the tip, is then inserted into the hole and fastened, and the spring compression is adjusted to provide a nominal contact pressure between the probe and the absorber.

A simple alternative that may be practicable in some instances is to push a thermocouple sensor behind the absorber plate from the hole in the side of the collector casing through which the humidity meter was inserted.

4.3.3 Absorber interior

At TÜV Bayern e.V. [4] it has been found that a quick and accurate means of obtaining an average absorber temperature under stagnation is to measure the saturation vapour pressure of water or some other liquid introduced into the empty absorber.

4.4 Atmospheric pollutants

The measurement of atmospheric pollutants, which typically have concentrations of few parts per million or per billion, requires sensitive instrumentation and precise techniques of chemical analysis. Solar testing laboratories may therefore prefer to make use of routine monitoring by environmental agencies or to specify the the quality of air by some descriptive means such as corrosion classes. The following account of quantitative methods of measuring pollutants is accordingly only brief.

For terminology and units of measurement ISO standards may be consulted [5] [6]. There is also an ASTM standard on the terminology of atmospheric sampling and analysis [7].

4.4.1 Oxides of sulphur

For continuous monitoring of sulphur dioxide a wide variety of techniques may be employed, including conductivity, colorimetry, nondispersive-infrared, coulometry, spectrophotometry, flame-emission spectrometry, electrochemistry, ultraviolet absorption, titration, and condensation-nuclei methods. A great many commercial instruments are available. An account of these methods is given by Wark and Warner [8].

The national network of pollution monitoring stations in the Netherlands measures sulphur dioxide concentrations continuously using an ultraviolet-fluorescent technique. Another method common in Europe [8] is the hydrogen-peroxide method (based on acid titration). International standards for monitoring the concentration of sulphur dioxide have been published by the ISO [9] [10].

Of manual methods, the West-Gaeke (colorimetric) method has been adopted as standard by the US Environmental Protection Agency. A standard procedure for this method is given in ASTM Standard D 2914 [11].

A method for measuring the total oxides of sulphur in the atmosphere is specified in ASTM Standard D 2010 [12].

4.4.2 Oxides of nitrogen

Measurements of nitrous oxide (NO_2) concentrations in the air are generally carried out using chemiluminescence, colorimetric or coulometric methods. In the USA, colorimetric methods have been adopted as standards in California (the Griess-Saltzmann method) and by the Environmental Protection Agency (the Jacobs-Hochheiser method). The Griess-Saltzmann method is the basis of ASTM Standard D1607 [13].

The same techniques can be extended to measure concentrations of nitric oxide (NO). A separate sample in which the nitric oxide has been oxidized to nitrous oxide is tested and the difference in the results gives the nitric-oxide concentration. A procedure for a combined test for nitrogen oxides using the Griess-Saltzmann method is specified in ASTM Standard D 3608 [14]. In the Netherlands the oxides of nitrogen are monitored using chemiluminescence.

Wark and Warner [8] note that significant differences can occur between the results of different methods for measuring the oxides of nitrogen, so that care has to be taken in to ensure the validity of a particular choice of technique.

4.4.3 Ozone

Photochemical oxidants in the atmosphere are usually measured using chemiluminescence, although colorimetric and coulometric instruments are commercially available. When corrected for the presence of sulphur dioxide and nitrous oxide, the remaining photochemical-oxidant concentration is effectively that of ozone. An ASTM procedure for measuring the oxidant content of the air is specified in ASTM Standard D2912 [15].

4.4.4 Corrosion classes

For some purposes a qualitatitive classification of the environment may be an adequate description of its corrosive properties. The Danish Standard DS 4-12-1976, for example, provides the following corrosion classes:

Corrosion classes	Agressiveness of environment	Examples of environment
0	None	Indoors in dry rooms. (Relative humidity < 60%)
1	Insignificant	Indoors in non-heated but well-ventilated rooms.
2	Slight	Indoors with changing humidity. Outdoors, far from industrial and urban districts.
3	Severe	In industrial and urban districts. Above water and along the coast.
4	Very severe	In constantly moist surroundings. At chemical plants. Under water and in the ground.

A limitation of this particular classification for solar collector durability studies is that there are only two classes of environment (corrosion class 2 and corrosion class 3) in which the great majority of collectors are likely to be sited. As an aid to collector design, however, the idea of corrosion classes could provide a useful means of specifying worst-case conditions for collector endurance.

4.5 Ultraviolet radiation

Instruments useful for measuring radiation in the near-ultraviolet range (with wavelengths in the range of about 300 - 400 nm) are of two types: radiometers based on photoelectric cells, and solid-state detectors. The radiometers have to be mounted apart from the collector, and they monitor the radiation incident on the collector surface. To find the radiation on the inside surfaces of the collector these measurements would have to be combined with measurements of the ultraviolet transmittance of the covers. The solid-state detectors, on the other hand, are sufficiently small to be placed inside a collector if necessary.

Instead of measuring ultraviolet radiation it may in some countries be possible to utilize regularly monitored data from meteorological offices or other radiation monitoring agencies.

4.5.1 Radiometers

Commercial radiometers for measuring global radiation in the near-ultraviolet region are similar in construction and operation to pyranometers but incorporate a special filter to remove the visible part of the spectrum. Two commonly used instruments are the (US-made) Eppley UV radiometer and the (Australian) CN ultraviolet pyranometer, which have similar designs based on selenium barrier-layer photoelectric cells. The sensor is protected by a sealed-in quartz window. In the Eppley instrument the standard interference filter has a bandpass of 295-385 nm, and in the CN instrument a glass filter gives a similar range of 290-385 nm. In both instruments an opaque quartz diffusing disk is used to attenuate the flux on the sensor and to ensure a Lambert cosine-law angular dependence.

The sensitivities of these radiometers is of order 0.10 - 0.15 mV/(W m^{-2}), and the calibration accuracy claimed for them is in the region of 5 - 10%. The Eppley radiometer is calibrated by the manufacturer, outdoors for the broad band-pass instrument and by reference to a calibrated thermopile. A calibration certificate authorised by the Australian National Association of Testing Authorities is provided with the CN instrument.

4.5.2 Solid-state detectors

Semiconductor ultraviolet sensors are also commercially available. No experience with such instruments is reported by Task III participants, however.

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American Society for Testing and Materials, 1916 Race St, Philadelphia, PA 19103

5 DURABILITY STUDIES

5.1 Field and laboratory tests

Durability tests are performed by indoor or outdoor exposure of either complete collector modules or material samples. Degradation of complete modules is generally assessed by measurements of thermal performance or of stagnation temperatures, whereas the degradation of samples can be determined from measurements of optical or mechanical properties or by measurements of the extent of corrosion.

5.1.1 Whole-collector durability tests

A standard practice for exposure testing of solar collectors is recommended by ASTM Standard E 823 [1], which provides for exposure to stagnation conditions either outdoors or in a simulated outdoor environment. The standard specifies an exposure of at least 30 days with a minimum cumulative irradiation of 17 $MJ/(m^2 \; day)$, during which period combined thermal-shock and water-penetration qualification tests are carried out. The effects of the exposure on the test collector are reported as visual changes revealed by inspection and changes in the thermal-performance characteristic measured according to ASHRAE Standard 93-77 [2].

An analysis of the results of an extensive reliability/durability test programme conducted by the US National Bureau of Standards cast serious doubt on the value of this form of test. Recently-published conclusions from the programme [3] suggest that the changes in material properties that typically follow even 480 days of outdoor exposure to an irradiation of 17 $MJ/(m^2 \; day)$ cannot be adequately detected by either thermal-performance measurements or stagnation-temperature measurements. Over a period of about three years the change in the pyranometer calibration might be of the same order as the change in the collector efficiency.

5.1.2 Cover materials

Samples of cover materials mounted in small weathering boxes and exposed to outdoor conditions are commonly used in durability studies. For testing under simulated operational conditions ASTM Standard E 782 [4] provides a recommended practice, while for testing under stagnation conditions there are recommendations in ASTM Standard E 881 [5]. The optical properties of the cover materials before and after exposure can be measured according to the methods outlined in 3.1.1 - 3.1.3 above.

ASTM Standard E 765 [6] specifies a number of qualification tests for solar collector glazing materials. These include outdoor exposure, either to natural weathering or to the accelerated weathering of concentrated sunlight and intermittent water sprays, and indoor exposure to high temperatures and xenon-arc radiation with water sprays. To determine the effects of the weathering, the standard recommends measurement of the solar transmittance, hail-impact resistance, dimensional stability, and tensile properties. Recent proposals for revisions of ASTM Standard E 765 encourage the use of normal and hemispherical spectral measurements of the solar transmittance rather than the integrated value [7]. Spectral measurements give a better indication of photo-oxidation and yellowing, and changes in the normal transmittance are more sensitive to the haze caused by crazing and cracking.

The NBS durability/reliability test programme revealed that the combination of high temperature, high humidity and high irradiance cause much more severe degradation than each of these conditions in isolation. An exposure to natural weathering of at least two years is needed to produce a level of degradation in polymers which can readily be observed, although the same effects can be induced in four months of exposure to a six-fold concentration of sunlight at elevated temperatures and with intermittent water spray. Outer-cover stagnation temperatures as high as 90 °C are necessary to obtain comparable results from indoor testing with xenon-arc radiation and water sprays. A much more rapid degradation occurs at this temperature than at the value of 75 °C specified in ASTM Standard E 765, and thermal modelling has shown that this value is more representative of extreme outdoor conditions. Proposals for improvements to ASTM Standards E 782 and E 765 have been made as a result of these observations [7].

5.1.3 Absorber coatings

ASTM Standard E 781 [8] provides a practice for testing absorber coating materials by outdoor exposure of samples fixed onto the absorber of a glazed and tightly-sealed collector. Stagnation conditions are maintained for a period over which the cumulative irradiation is at least 6.2 GJ/m^2 (about 12 months), and the degradation of the coating which results is inferred from changes in the appearance of the coating and in the integrated values of solar absorptance and infrared emittance.

Changes to ASTM Standard E 781 are proposed [7] to reflect the fact that spectral reflectance measurements give more information about degradation than integrated values. Also, moisture is common in solar collectors and a major factor contributing to degradation, and this effect is not shown up when the test specimens are mounted in well-sealed collector boxes.

Another recommended practice for testing the durability of absorber coatings is provided by ASTM Standard E 744 [9]. Method B of this standard is based on ASTM Standard E 781, while Method A specifies test conditions for simulating outdoor exposure tests in the laboratory. The indoor tests include a 500-hour exposure to stagnation temperatures, a 30-day exposure to 95% relative humidity at 90 °C, a 30-cycle exposure to thermal cycling between -10 °C and the stagnation temperature, and exposure to concentrated solar radiation or radiation from a carbon or xenon arc lamp. The effects on the absorber coating are determined according to ASTM Standard E 781.

The changes proposed for ASTM Standard E 781 are equally appropriate for ASTM Standard E 744. It is also recognized that the moisture exposure test is too severe, producing much greater changes than would be seen in a normal exposure of three years. In addition, the use of the carbon-arc lamp is no longer recommended.

Other methods used by Task III participants for studying the degradation of absorber coatings include electron microscopy to examine structural changes, and mass spectrometry to reveal any migration of chemical elements.

5.1.4 Heat-transfer-fluid compatability

A review of ASTM standard practices for screening metals and polymers for compatability with heat-transfer fluids is given by Waksman [7]. For metals ASTM Standard E 712 [10] provides six test procedures:

> In Method A the metal and the fluid are held at the same temperature, so that no heat transfer takes place between them. It is intended to reveal the corrosion that would take place in tanks and piping rather than within the collector fluid ducts.
>
> Method B is intended to simulate the conditions within the collector, where the heat transfer between the metal and the fluid can strongly influence the rate of corrosion. The fluid is in free contact with the atmosphere, so the results apply only to open systems.
>
> Method C simulates the stagnation conditions of a full, partially-filled, or empty collector installed in a closed (pressurized) loop.
>
> Method D simulates the conditions inside a collector in an open-loop system with drain-down, where there is repeated wetting and drying.
>
> Method E, which is based on ASTM Standard G 48 [11], is used to test for crevice corrosion in collectors.
>
> Method F applies to collectors in open systems, like Method B, but takes into account the influence of curvature in the metal, so it is more applicable to tubular fluid ducts.

To simulate the combined effects of stagnation and normal running conditions ASTM Standard E 745 [12] provides three tests for metal-fluid compatability:

> In Method A, sample coupons are tested with or without aeration to simulate conditions in open or closed systems. This method does not account for heat transfer to the fluid.
>
> Methods B and C test components and subcomponents in the laboratory and outdoors, respectively. In these tests the exposure to the fluid may be accompanied by a substantial transfer of heat.

The influence on polymer materials of exposure to heat-transfer fluids at the temperatures attained in operating conditions may be tested according to ASTM Standard E 862 [13]. The effects are observed as changes of appearance, dimensions, mass, and mechanical properties.

5.1.5 Gaskets and sealants

Specifications for rubber gaskets and sealants for use in flat-plate collectors, in concentrating collectors, in contact with heat transfer fluids, and in air systems are provided by ASTM Standards D 3667 [14], D 3771 [15], D 3832 [16], and D 3903 [17], respectively. The specifications set acceptable limits on the effects of high and low temperatures and ozone on the elastic and adhesive properties of the materials.

5.1.6 Hoses

In addition to the properties required for sealants, hoses need to have a resistance to bursting, vapour seepage, and chemical interactions with metals and heat-transfer fluids. A complete specification for hoses is recommended in ASTM Standard D 3952 [18]

5.1.7 Insulation materials

Standards for the resistance of insulation materials to physical and chemical changes caused by mechanical and thermal stress and moisture are recommended in ASTM Standard E 861 [19].

5.1.8 Metal casings and fixings

A recommended practice for conducting atmospheric corrosion tests on metals is provided by ASTM Standard G 50 [20]. The standard specifies criteria for the choice of test sites and for the construction and siting of exposure racks, for the form and preparation of test specimens, and for the evaluation and reporting of test results. To test the resistance of stainless steels and nickel-based chromium-bearing alloys to corrosion in oxidizing chloride environments, ASTM Standard G 48 [11] may be of use.

5.2 Observations and models of internal collector environments

The use of the results of environmental tests on material samples to estimate the durability of the materials within a collector requires an understanding of the microclimate within the collector during normal operation and stagnation. Humidity, condensation and ventilation rates within the collector are interrelated and also depend dynamically on external meteorological variables such as rainfall, humidity, and the direction and strength of the wind. The following paragraphs summarize some interesting observations and models which cast light on these complex and still largely unpredictable phenomena.

Measurements of the environmental variables of collectors - internal and external - have been reported by Vejsig Pedersen [21] and Marshall [22]. Vejsig Pedersen was concerned with the effect of ventilation on condensation in the collector. This topic is treated in 5.2.1. The work of Marshall, which was undertaken for the CEC Collector and System Testing Group, was directed towards finding correlations between the internal environmental variables of the collector and the external, meteorological variables. Some of the conclusions from this investigation are summarized in 5.2.2.

5.2.1 Moisture and ventilation in collectors

In his study of moisture and ventilation in collectors, Vejsig Pedersen [21] monitored the temperature and relative humidity inside collectors in stagnating conditions. The solar radiation, ambient temperature and ambient relative humidity were also recorded.

At the start of the programme ventilation rates through the collectors had been measured with over- and under-pressures of up to 300 Pa. This was done by connecting a vacuum cleaner and precise manometers to holes in the collector casing. The collectors were then classified into three different ventilation groups according to whether the ventilation rate per 100 Pa was less than 1 m^3/h, 1 - 20 m^3/h, or greater than 20 m^3/h. Although the pressure differences due to wind and convection in normal operation are of order 1 - 3 Pa, which cannot be measured in practice, this classification provided a measure of the air-tightness of the collectors that could be correlated with observations of condensation during stagnation.

In another form of classification, the collectors were separated into types according to whether there were ventilation holes in the bottom edge of the collector only, at the top and bottom, or in the back of the collector (behind the insulation). In field trials it was observed that the collectors with ventilation holes at the back rarely showed condensation and that the humidity inside these collectors was usually lower than the ambient humidity.

In general, only evacuated collectors are completely free of condensation; an almost air-tight collector will eventually become wet inside, and then it is unlikely to dry because there is insufficient ventilation. A simple dynamic model of how moisture accumulates in such a collector as a result of diurnal temperature cycles is given in a paper by Samuelson [23]. Water vapour is drawn into the collector with the ambient air as the collector cools and is expelled with the expanded air as the collector warms. However, the water which has condensed inside the cold collector does not re-evaporated instantly, and thus the outgoing air may be drier than it would be in equilibrium. The result is a net influx of water.

5.2.2 Monitoring of internal and external collector environments

In the study by Marshall, probes were installed inside four collectors to measure humidity and air temperature, moisture, and absorber surface temperatures. The internal variables were then monitored over a period of twelve months, together with the ambient temperature, ambient humidity, irradiance, and windspeed. Data were recorded at five-minute intervals and formed into hourly-averaged values. The study thus provided a large data bank with which to look for correlations between the internal and external variables.

Some general observations from the study [22] were that the humidity inside the collectors was usually much higher than the ambient humidity, often greater than 50%, but that the absorbers remained dry irrespective of the external variables, even when the internal humidity was 100% and there was condensation on the inside of the glazing. Although the internal humidity and temperatures followed the irradiance as expected, the relationship provided no simple model for the behaviour of the internal variables. Marshall concluded that a detailed model with two-phase heat and mass transfer would be necessary to describe the processes of humidity change and moisture condensation within the collector.

5.3 Conclusions and recommendations

While we are far from the ideal of being able to predict for a collector with a specific design and construction the probability of its having a given useful lifetime, this report has shown that much has already been achieved.

We have the means to quantify and measure the different forms of material degradation that affect durability, as well as the internal and external environmental variables which influence degradation. We have more information on the value and interpretation of environmental exposure tests, and are beginning to understand the implications of short-term, accelerated aging tests for the degradation in actual service.

More information is available on the microclimate within collectors, and we can therefore say something about the corrosive conditions which collector materials have to endure. However, it has not been found practicable to develop models of the internal microclimate and its relation to external variables.

In order to provide advice on how to avoid failure in collectors, more research is needed on design features that would improve the durability. A further study of ventilation in collectors might, for example, give information on the best size and positions of ventilation holes to minimize condensation.

A search for new materials might provide examples which are inexpensive but have a better resistance to degradation. Advice is needed on the optimum combination of materials in collectors, such as heat-transfer fluids and fluid conduits. And it may be that the durability of materials or collector modules can be improved in the manufacturing process.

Answers to these questions would contribute much to the viability of active solar energy.

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Subtask E : Development of a Capability to Evaluate Domestic Hot Water System Performance using Short - Term Test Methods

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