



**EFFECTIVENESS OF USING PURE COPPER AND SILVER
COUPON CORROSIVITY MONITORING (CCM) METAL STRIPS
TO MEASURE THE SEVERITY LEVELS OF AIR POLLUTANTS IN
INDOOR AND OUTDOOR ATMOSPHERES**

L Jay Foax (LJFoax@csir.co.za) and *Nonjabuliso Mazibuko*,
Council for Scientific and Industrial Research (CSIR),
Corner Frost Avenue and Menton Road, Auckland Park,
Johannesburg, South Africa.

ABSTRACT

Severity levels of air pollutants rich in oxides, chlorides and sulphides were successfully measured in indoor and outdoor atmospheres using pure copper and silver coupon corrosivity monitoring (CCM) metal strips when the maximum exposure periods were limited to thirty days for indoor and ninety days for outdoor environments. Resultant corrosion products from air pollutants which were successfully measured were copper oxides (CuO and Cu₂O), copper sulphides (Cu₂S), silver chlorides (AgCl) and silver sulphides (Ag₂S). The total film thickness measured for copper corrosion products were as low as 36Å for indoor atmospheres (G1, mild) and as high as 6019Å for outdoor atmospheres (GX, severe). The total film thickness measured for silver corrosion products were as low as 98Å for indoor atmospheres (G1, mild) and as high as 3464Å for outdoor atmospheres (GX, severe). Coulometric/cathodic reduction current densities used for both copper and silver were 0.05mA/cm² (indoors) and 0.5mA/cm² (outdoors). Coulometric/cathodic reduction potentials for CuO were between minus 0-600mV, between minus 600-900mV for Cu₂O and between minus 900-1200mV for Cu₂S. AgCl was reduced between minus 0-700mV and Ag₂S between minus 700-1200mV. The hydrogen evolution stages for both copper and silver were observed at -1200mV for indoor and -800mV for outdoor environments.

Keywords: Air Pollutants, Corrosion Products, Oxides, Chlorides, Sulphides, Coulometric/cathodic Reduction, Film Thickness, Copper and Silver Coupon Corrosivity Monitoring (CCM) Metal Strips, Scanning X-Ray Photoelectron Spectroscopy (SXPS)

INTRODUCTION

Air pollutants rich in oxides, chlorides and sulphides can cause severe corrosion of various alloy materials in many industrial components. Replacement costs for the alloy materials and these components (such as PC boards of many industrial instruments) can be extremely high. Modern techniques of monitoring the severity levels of air pollutants may be costly and out of reach for many developing countries. There is a need to continuously investigate the effectiveness of cheaper

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alternative techniques and compare results with those of modern techniques. This publications aims to show that the severity levels of air pollutants in indoor and outdoor atmospheres could be accurately determined by the exposure, testing and analysis of pure copper (Cu) and silver (Ag) coupon corrosivity monitoring (CCM) metal strips, when the maximum exposure periods are limited to thirty (30) days for indoor atmospheres and ninety (90) days for outdoor environments. The CCM atmospheric corrosion test has proven to be an effective, rapid and low-cost test for specific micro-environments in South African industries, such as different areas of the cities, control rooms of industrial plants, hangars of military installations or industrial sites known to continually generate air pollutants. The CSIR has successfully used the CCM technology to aid in alloy materials selection, coating materials selection (such as roofing materials and metallic coatings), atmospheric corrosion failure investigations and air quality monitoring to improve the service life of filter packs in air treatment plants.

EXPERIMENTAL PROCEDURE

Chemical composition analysis of metal strips was carried out to confirm the composition make-up of the alloy materials. The Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) technique was used for chemical composition analysis. Copper (Cu) CCM metal strips were prepared from half hard, high purity, oxygen-free high conductivity (OFHC) copper. Silver (Ag) CCM metal strips were prepared from high purity silver. Dimensions of the metal strips used were 75mm (length) x 10mm (width) x 1mm (thickness), with 4mm holes spaced 65mm apart (see **Figure 1**).

Metallographic Preparation

Special sample holders were prepared to hold metal strip specimens during metallographic preparation. Metallographic preparation, i.e. manual grinding and polishing of metal strip specimens was carried out using basic guidelines and procedures defined by the ASTM E3^[1] specification. Grinding of both sides of the metal strip was carried out using the 240 grit, 320 grit and 600 grit abrasive paper with liquid paraffin as the lubricant. Polishing of one side of the metal strip was carried out using a napped polishing cloth, 6µm diamond paste and light paraffin as a lubricant. Care was taken to avoid scratches on metal strip surfaces and contamination during sample preparation. Metal strip specimens were stored in warm isopropyl alcohol ((CH₃)₂CHOH) during various metallographic sample preparation stages. Cleaning of metal strip specimens in-between the preparation stages was carried out in hot reagent grade acetone (CH₃COCH₃), in an ultrasonic bath. Cotton wool soaked in the acetone was used to remove adherent materials from one preparation stage to another.

Storage, Assembly and Packaging

Specimens were stored prior to their assembly in a glass container filled with isopropyl alcohol, purged with dry high purity nitrogen. Specimens were then removed from the isopropyl alcohol using forceps, held on the edges, dried and mounted on perspex holders. Perspex spacers were used to position the metal strip in the middle of the holder (see **Figure 1**). A label was attached on the perspex holder of each specimen. Appropriate hand gloves were used during the handling of specimens. The assembled specimens were sealed in dry high purity nitrogen in a multi-layer foil laminated sachets. Each sachet was constructed from the material with exceptionally low gas and moisture permeability. Suitable, field sealable sachets with silica gel crystals were supplied with CCM specimens for their return to the CSIR after atmospheric exposure.

Atmospheric Exposure

Indoor CCM metal strip specimens were exposed in an industrial control room environment where the air was filtered and the operating conditions were controlled by an air conditioner. Outdoor CCM metal strip specimens were exposed to the external weather conditions at various locations of the greenhouse farm where severe corrosion of galvanized steel components was observed. At the site being monitored, specimens were removed from the multi-layer foil laminated sachets and installed vertically to the target environment. The exposure site descriptions and exposure periods were recorded on the labels of specimens. Installation of specimens was carried out in areas with free air circulation and which have air flow rates that are characteristic of the site. Particular care was taken to ensure that CCM metal strip specimens in indoor atmospheres were sheltered from outdoor weather variables and that surface contamination such as fingerprints was avoided. Specimens were removed from the indoor exposure sites after thirty (30) days of continuous exposure. CCM metal strip specimens in outdoor atmospheres were removed from the site after ninety (90) days of continuous exposure. Depending on the severity level ranking of the target atmosphere, exposure periods of CCM metal strip specimens in both indoor and outdoor atmospheres can be extended to the maximum of ninety (90) days in mild environments or reduced to the minimum of fourteen (14) days in harsh environments, so long as measurements over longer or shorter times were reduced to the normalized exposure period of thirty (30) days by using an exposure time standardization relationship formula defined by the ISA-S71.04^[4] standard:

$$x_1 = \left(\frac{t_1}{t} \right)^A \quad (1)$$

where: x_1 is the equivalent film thickness after thirty (30) days of exposure,
 x is the measured film thickness after exposure time t ,
 t_1 is thirty (30) days,
 t is the actual exposure time in days, and
 A is equal to 0.3 for G1, 0.5 for G2, 1 for G3 and GX.

After exposure, specimens were placed in their field sealable sachets with silica gel crystals and returned to the CSIR for testing and detailed analysis.

Scanning X-Ray Photoelectron Spectroscopy (SXPS) Analysis

Scanning X-ray Photoelectron Spectroscopy (SXPS) analysis consists of irradiating a surface with X-rays in order to extract photo-electrons. Knowing the energy of the X-ray photons and measuring the kinetic energy of the extracted electrons, one can determine the binding energy of the extracted electrons. This quantity is unique and can be used to identify the elements from which the electrons were extracted. The technique can detect all of the elements except hydrogen and helium, as well as compounds, because the binding energy of an element differs from compound to compound. It is primarily a surface technique, as the escape depth of the photo-electrons ranges from 2 to 5 nm. The detection limit of SXPS is approximately 0.1 atomic%. Information from subsequent layers beneath the outer surface can be obtained by sputtering the surface with energetic argon ions, while monitoring the binding energy regions of specific elements. The samples were sputtered for 1 minute to remove surface contamination. The experimental setup parameters used were: X-rays: Al K α (1486eV); X-ray

Power: 20 W; Beam Diameter: 100 μm ; Pass Energy (Wide): 117,4 eV and Pass Energy (Narrow): 29,35 eV.

SXPS wide scans were carried out on CCM metal strip specimens to determine the surface compositions, depth profiling and the thickness of films. Linear background subtraction and a least-square fitting were used to determine the peak positions, line-widths and peak areas. The semi-quantitative atomic percentage values were calculated from the peak areas for each element on the wide scans.

Coulometric/Cathodic Reduction of Surface Films

Coulometric/cathodic reduction of films developed on the surfaces of CCM metal strip specimens was carried out using test procedures defined by the ASTM B825^[2] specification and guidelines from the published literature^[3]. All tests were carried out in a de-aerated solution of 0.1 mol dm⁻³ potassium carbonate (K₂CO₃), at the temperature of 25°C. The coulometric/cathodic reduction plots/ potential-time curves were recorded after applying a constant current density using a Princeton M273TM potentiostat. Each plateau on the potential-time curves was identified and related to a corrosion product compound defined by the SXPS technique. Using the elapsed time from the recorded coulometric/cathodic reduction plots, the mass and thickness values of the surface films were calculated using Faraday's laws and formulae described in the ASTM B825^[2] specification:

- Mass of the known substances, W was calculated by the formula:

$$W = it \frac{10^3 M}{NF} \quad (2)$$

where:

- W = mass, μg ;
- I = current, mA;
- T = time, s, to reduce a known substance;
- M = gram-molecular weight of that substance, g;
- F = Faraday's constant ($9.65 \times 10^4 \text{ C}$); and
- N = Number of faradays required to reduce a gram-molecular weight of the substance, e.g. 1 for AgCl, 2 for Ag₂S, CuO, Cu₂O and Cu₂S.

- The equivalent film thickness of the known substances, T was calculated by the formulae:

$$T = \frac{itK}{a} \quad (3)$$

where

$$K = \frac{10^5 M}{NFd} \quad (4)$$

and:

- T = Thickness, Å (10^{-8} cm);
- I = current, mA;
- T = time, s, to reduce a known substance;
- A = Area of tested specimen, cm^2 ;
- F = Faraday's constant (9.65×10^4 C);
- D = density of substance being reduced, g/cm^3 ; and
- K = conversion factor,
e.g. 26.71 for AgCl, 17.54 for Ag₂S, 6.44 for CuO, 12.36 for Cu₂O and 14.73 for Cu₂S.

RESULTS AND DISCUSSION

Typical Chemical Composition

The typical chemical composition of the pure copper and silver coupon corrosivity monitoring (CCM) metal strips shown in **Table 1** (below) were considered to satisfy the high purity requirements for this test method.

Table 1: Typical Chemical Composition of the Copper and Silver Metal Strips

ALLOYING ELEMENT	CHEMICAL COMPOSITION (Weight %)	
	Copper Metal Strip	Silver Metal Strip
Aluminium, Al	≤0.002	≤0.002
Arsenic, As	0.006	≤0.002
Berillium, Be	≤0.002	≤0.002
Bismuth, Bi	0.004	≤0.002
Cobalt, Co	≤0.002	≤0.002
Iron, Fe	0.026	0.016
Manganese, Mn	≤0.002	≤0.002
Nickel, Ni	≤0.005	≤0.002
Phosphorus, P	0.385	≤0.002
Lead, Pb	0.417	≤0.002
Antimony, Sb	0.007	≤0.002
Silicon, Si	0.258	0.284
Tin, Sn	≤0.002	≤0.002
Zinc, Zn	≤0.002	≤0.002
Copper, Cu	Remainder	0.011
Titanium, Ti	--	1.38
Silver, Ag	--	Remainder

Scanning X-ray Photoelectron Spectroscopy (SXPS) Analysis

The following composition analysis was carried out on the surfaces of the pure copper and silver coupon corrosivity monitoring (CCM) metal strips to identify the corrosive species involved (see **Table 2** below):

Table 2: Typical SXPS Composition Analysis of the Copper and Silver Metal Strips

Sample	Element	Concentration (atom%)
Copper Coupon Corrosivity Monitoring (CuCCM) Metal Strip	Copper, Cu	37.1
	Chlorides, Cl	2.0
	Oxygen, O	42.0
	Sulphur, S	1.9
	Carbon, C	37.1
Silver Coupon Corrosivity Monitoring (AgCCM) Metal Strip	Silver, Ag	52.1
	Chlorides, Cl	1.9
	Oxygen, O	15.4
	Sulphur, S	1.9
	Carbon, C	28.8

The binding energies of the compounds formed were used to identify the main corrosive species from air pollutants involved. The main air pollutants detected in both indoor and outdoor environments were rich in oxides, chlorides and sulphides.

Coulometric/Cathodic Reduction of Surface Films

Coulometric/cathodic reduction current densities of $0.05\text{mA}/\text{cm}^2$ (indoor environments) and $0.5\text{mA}/\text{cm}^2$ (outdoor environments) were successfully used for the reduction of oxide, sulfide and chloride films on abraded copper and silver metal strips. The coulometric/cathodic reduction test method was successfully used to measure the film thickness of corrosion products: copper oxides (CuO and Cu_2O), copper sulphides (Cu_2S), silver chlorides (AgCl) and silver sulphides (Ag_2S) when both copper and silver are exposed to the same environment at the same time. From the same environment, silver (Ag) was sensitive to chlorides and sulphides whereas copper (Cu) was more reactive to oxides and sulphides. Each plateau on the coulometric/cathodic reduction potential-time plot was identified and related to a corrosion product compound defined by the Scanning X-ray Photoelectron Spectroscopy (SXPS) technique. On the copper metal strip surface, the first compound reduced between minus 0-600mV was copper oxide (CuO), followed by cuprous oxide (Cu_2O) which reduced between minus 600-900mV and copper sulphide (Cu_2S) which reduced between minus 900-1200mV. The hydrogen evolution stage was observed at minus 1200mV for indoor environments and minus 800mV for outdoor environments. On the silver metal strip surface, the first compound reduced between minus 0-700mV was silver chlorides (AgCl) followed by silver sulphides (Ag_2S) which reduced between minus 700-1200mV. The hydrogen evolution stage for silver was observed at minus 1200mV for indoor environments and minus 800mV for outdoor environments. The total copper film thickness values measured were as low as 36\AA for indoor atmospheres (G1, mild) and as high as 6019\AA for outdoor atmospheres (GX, severe). The total silver film thickness values measured were as low as 98\AA for indoor atmospheres (G1, mild) and as high as 3464\AA for outdoor atmospheres (GX, severe). Typical surface film thickness values measured by the coulometric/cathodic reduction method in indoor and outdoor environments on copper and silver metal strips are shown in **Table 3** (below):

Table 3: Typical Surface Film Thickness Measurements on Copper and Silver Metal Strips

Material ID	Sample ID	Surface Film Thickness, angstroms (Å)						ISA Severity Ranking**	Environment
		CuO	Cu ₂ O	Cu ₂ S	AgCl	Ag ₂ S	Total		
Copper Coupon Corrosivity Monitoring (CuCCM) Metal Strip	CuCCM-01	--	13	23	--	--	36	G1, Mild	Indoors
	CuCCM-02	110	3770	--	--	--	3880	GX, Severe	Outdoors
	CuCCM-03	148	2929	--	--	--	3077	GX, Severe	Outdoors
	CuCCM-04	241	5778	--	--	--	6019	GX, Severe	Outdoors
Silver Coupon Corrosivity Monitoring (AgCCM) Metal Strip	AgCCM-01	--	--	--	25	73	98	G1, Mild	Indoors
	AgCCM-02	--	--	--	1977	1052	3029	GX, Severe	Outdoors
	AgCCM-03	--	--	--	414	175	589	G2, Moderate	Outdoors
	AgCCM-04	--	--	--	2938	526	3464	GX, Severe	Outdoors

** Instrument Society of America Standard ISA-S71.04-1985

Classification/Ranking of Severity Levels of Air Pollutants

Guidelines from the ISA-S71.04^[4] standard were used to classify the measured thickness of air pollutants into the various severity level rankings:

- Severity Level Ranking: G1 (Thickness of 0-300 Å)
Environment Description: Mild – An environment sufficiently well-controlled such that corrosion is not a factor in determining equipment reliability.
- Severity Level Ranking: G2 (Thickness of 300-1000 Å)
Environment Description: Moderate – An environment in which the effects of corrosion are measurable and may be a factor in determining equipment reliability.
- Severity Level Ranking: G3 (Thickness of 1000-2000 Å)
Environment Description: Harsh – An environment in which there is a high probability that corrosive attack will occur. These harsh levels should prompt further evaluation resulting in environmental controls or specially designed and packaged equipment.
- Severity Level Ranking: GX (Thickness ≥2000 Å)
Environment Description: Severe – An environment in which only specially designed and packaged equipment would be expected to survive. Specifications for equipment in this case are a matter of negotiation between user and supplier.

CONCLUSIONS

Severity levels of air pollutants rich in oxides, chlorides and sulphides were successfully measured in indoor and outdoor atmospheres using pure copper (Cu) and silver (Ag) coupon corrosivity monitoring (CCM) metal strips when the maximum exposure periods were limited to thirty (30) days for indoor and ninety (90) days for outdoor environments. Air pollutants which were successfully identified and

measured were rich in oxides, sulphides and chlorides; as indicated by the corrosion products: copper oxides (CuO and Cu₂O), copper sulphides (Cu₂S), silver chlorides (AgCl) and silver sulphides (Ag₂S). The copper and silver CCM technique of measuring the severity of air pollutants (by measuring the film thickness of resultant corrosion products) had proven to be a relatively rapid, cost-effective and accurate means of providing information that can be used to minimize atmospheric corrosion effects on metallic materials, machinery and plant infrastructure by taking appropriate corrective measures.

ACKNOWLEDGEMENT

The Council for Scientific and Industrial Research (CSIR) is acknowledged for financial support and permission to publish test methods and results.

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1. ASTM E3: Standard Practice for Preparation of Metallographic Specimens; American Society for Testing and Materials (ASTM); 1995.
2. ASTM B825: Standard Test Method for Coulometric Reduction of Surface Films on Metallic Test Samples; ASTM; 1997.
3. Campbell WE and Thomas UB; *“Tarnish Studies: The Electrochemical Reduction Method for the Analysis of Films on Metallic Surfaces”*; General Meeting of the Electrochemical Society; New York; September 1939.
4. ISA-S71.04-1985: ISA Standard – *“Environmental Conditions for Process Measurement and Control Systems: Airborne Contaminants”*; Instruments Society of America (ISA); 1985.

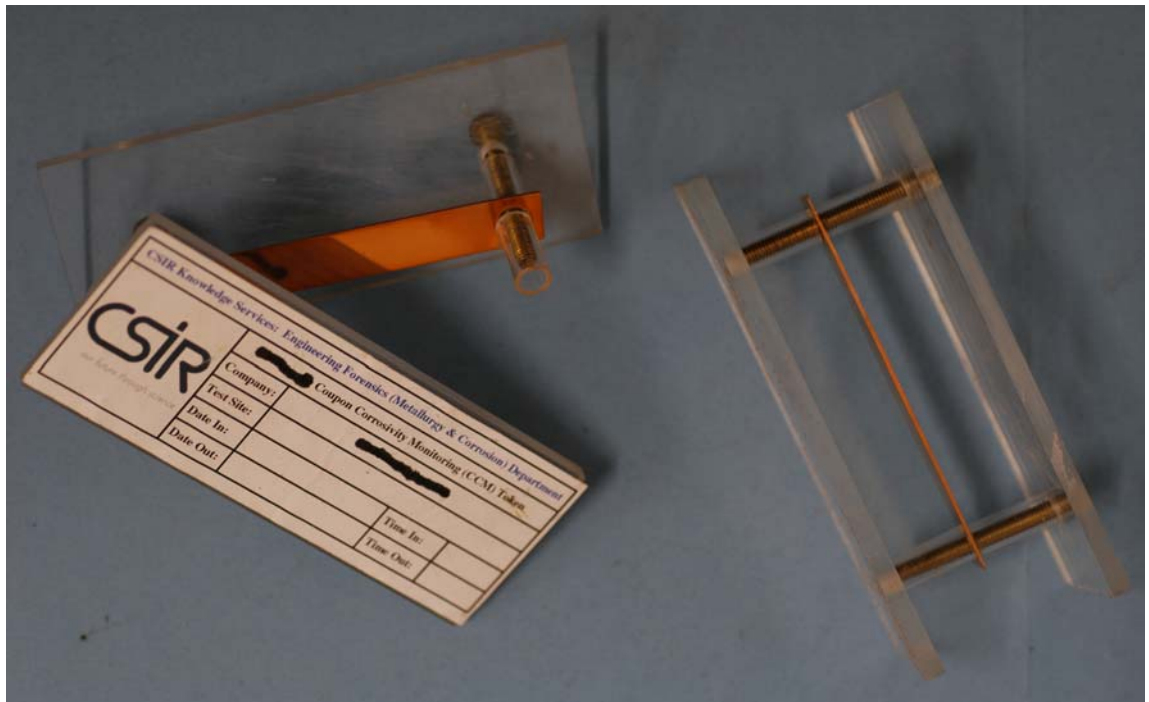


Figure 1: General appearance of construction materials for the Coupon Corrosivity Monitoring (CCM) metal strips used by the CSIR to measure the severity levels of air pollutants in indoor and outdoor environments, by measuring the film thickness of resultant corrosion products.

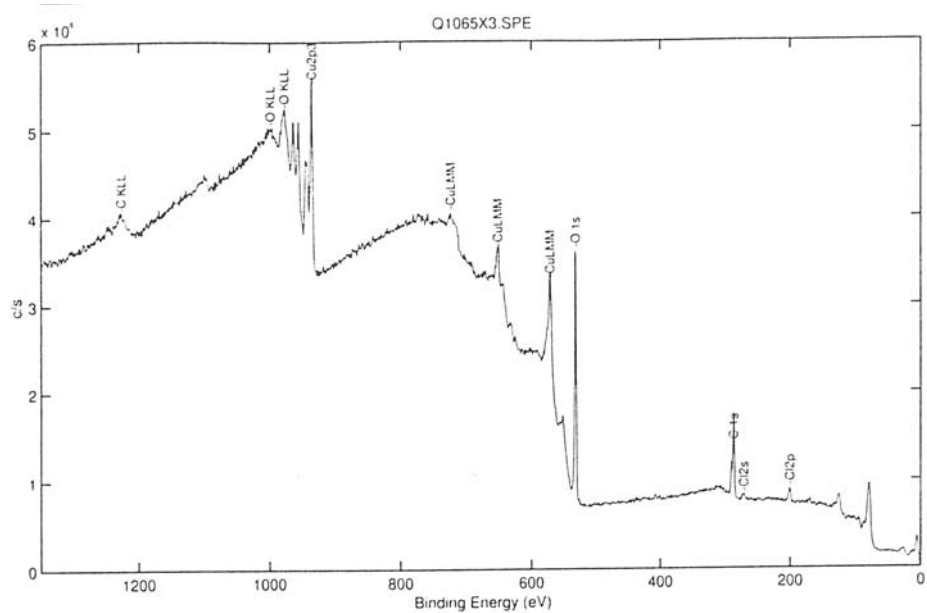


Figure 2:

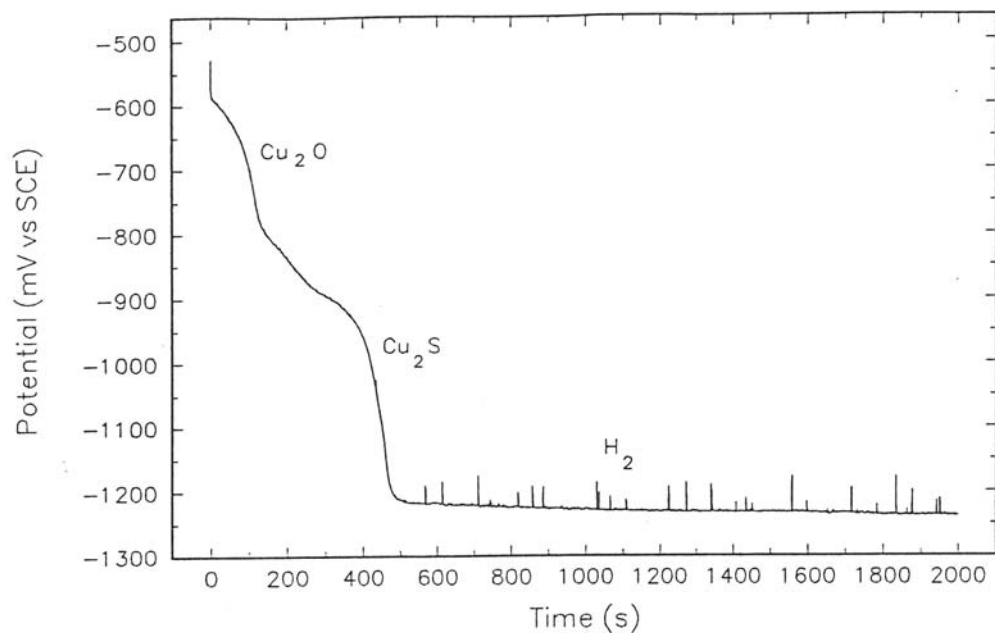


Figure 3:

Figures 2-3: The typical Scanning X-ray Photoelectron Spectroscopy (SXPS) spectrum (Fig. 2) and corresponding coulometric/cathodic reduction plot (Fig. 3) derived from testing the surfaces of the pure copper coupon corrosivity monitoring metal strip exposed to an indoor atmosphere over a period of 30 days. Air pollutants detected in this indoor environment were rich in mainly oxides, chlorides and sulphides. The coulometric reduction current density used for this indoor environment was 0.05mA/cm^2 . The total film thickness measured by use of the coulometric/cathodic reduction technique was 36\AA (13\AA for Cu_2O and 23\AA for Cu_2S). The severity level ranking of air pollutants was classified as G1 (mild environment).

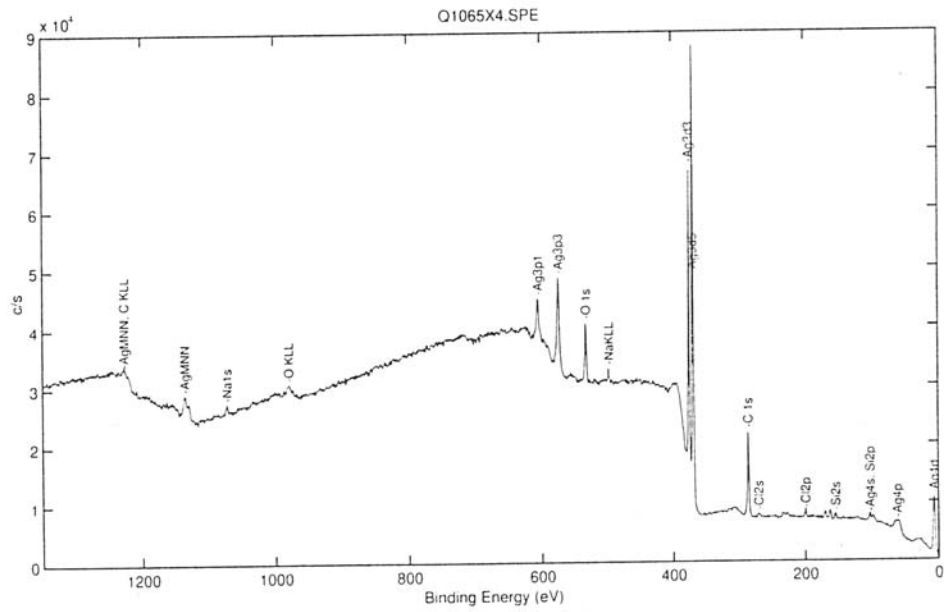


Figure 4:

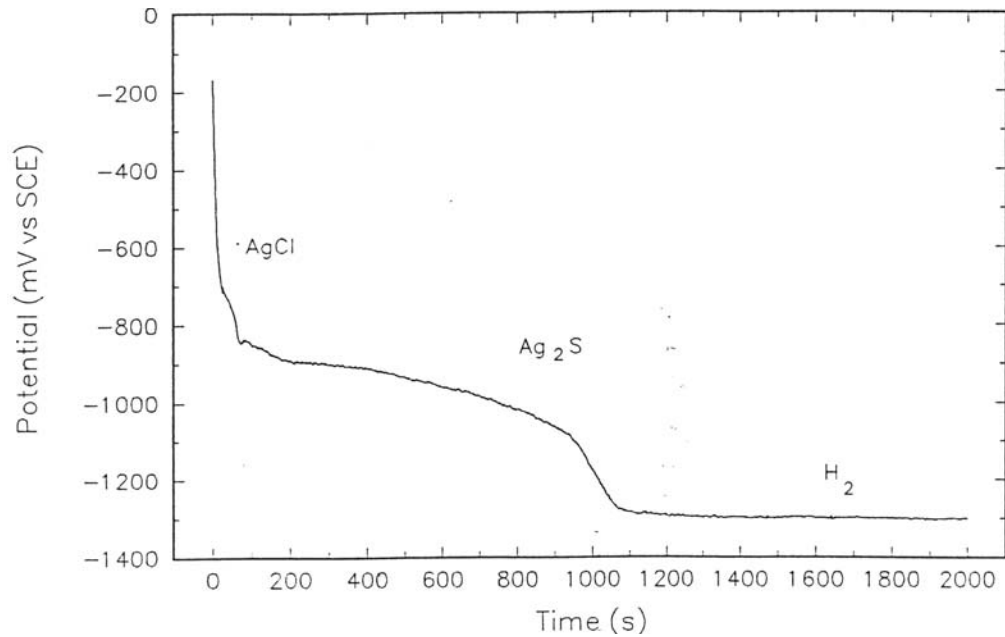


Figure 5:

Figures 4-5: The typical Scanning X-ray Photoelectron Spectroscopy (SXPS) spectrum (Fig. 4) and the corresponding coulometric/cathodic reduction plot (Fig. 5) derived from testing the surfaces of the pure silver coupon corrosivity monitoring metal strip exposed to an indoor atmosphere over a period of 30 days. Air pollutants detected in this indoor environment were rich in mainly oxides, chlorides and sulphides. The coulometric reduction current density used for this indoor environment was $0.05\text{mA}/\text{cm}^2$. The total film thickness measured by use of the coulometric/cathodic reduction technique was 98\AA (25\AA for AgCl and 73\AA for Ag_2S). The severity level ranking of air pollutants was classified as G1 (mild environment).

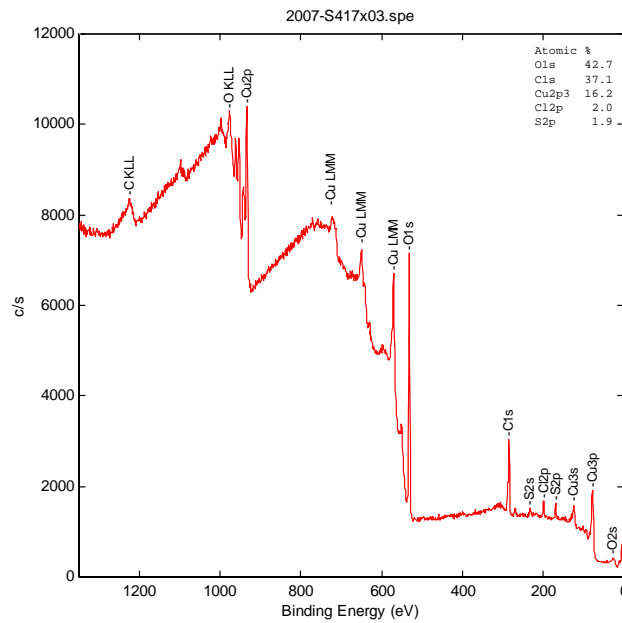


Figure 6:

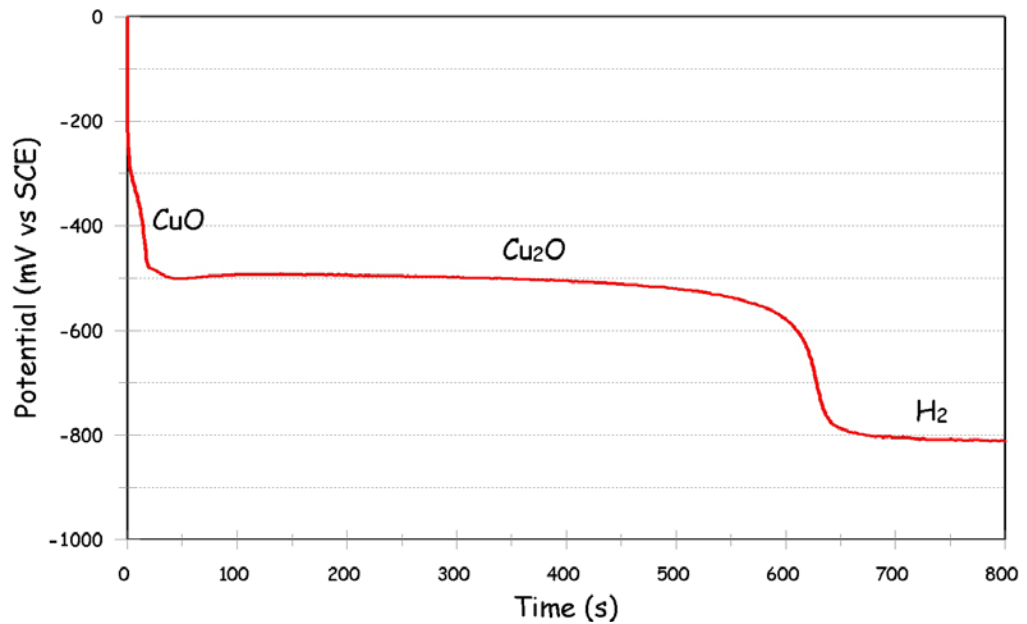


Figure 7:

Figures 6-7: The typical Scanning X-ray Photoelectron Spectroscopy (SXPS) spectrum (Fig. 6) and corresponding coulometric/cathodic reduction plot (Fig. 7) derived from testing the surfaces of the pure copper coupon corrosivity monitoring metal strip exposed to an outdoor atmosphere over a period of 30 days. Air pollutants detected in this outdoor environment were rich in mainly oxides, chlorides and sulphides. The coulometric reduction current density used for this outdoor environment was 0.5mA/cm^2 . The total film thickness measured by use of the coulometric/cathodic reduction technique was 3880\AA (110\AA for CuO and 3770\AA for Cu_2O). The severity level ranking of air pollutants was classified as GX (severe).

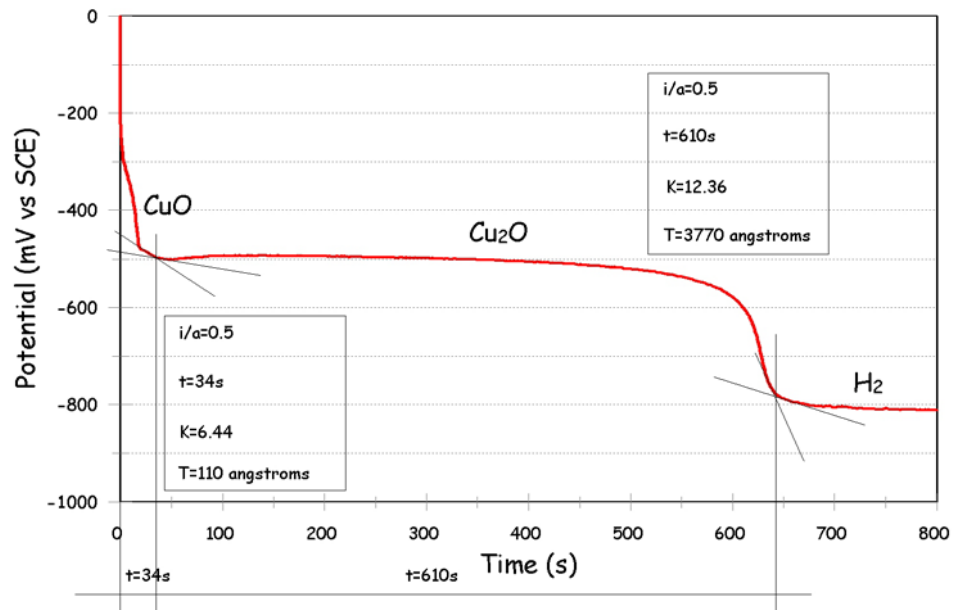


Figure 10:

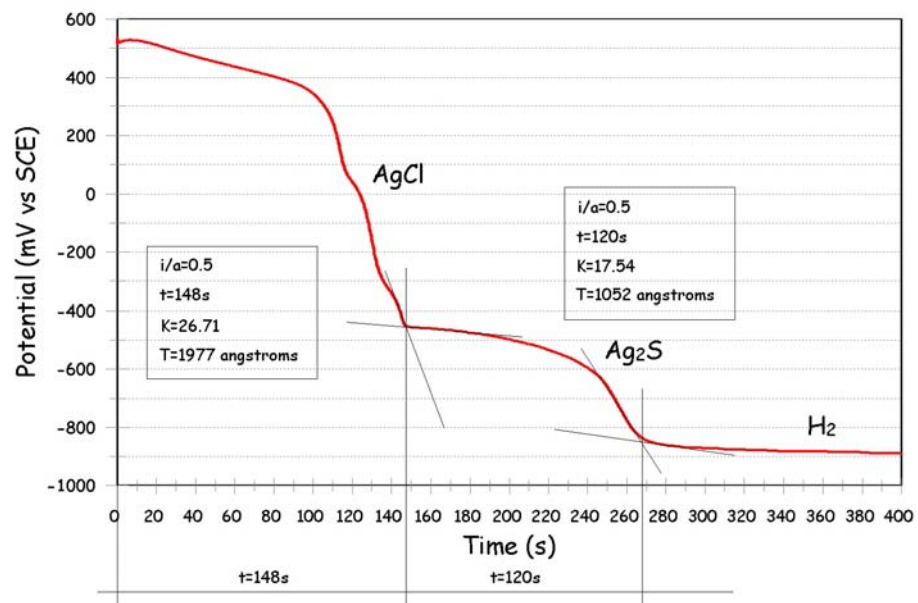


Figure 11:

Figures 10-11: The typical coulometric/cathodic reduction plots show how reduction times were extrapolated from inflection points of plateaus for different corrosion product species. Air pollutants detected in this outdoor environment were rich in mainly oxides, chlorides and sulphides. The coulometric reduction current density used for this outdoor environment was $0.5\text{mA}/\text{cm}^2$. The total film thickness measured for copper by use of the coulometric/cathodic reduction technique was 3880\AA (110\AA for CuO and 3770\AA for Cu_2O). The total film thickness measured for silver by use of the coulometric/cathodic reduction technique was 3029\AA (1977\AA for AgCl and 1052\AA for Ag_2S). The severity level ranking of air pollutants was classified as GX (severe).

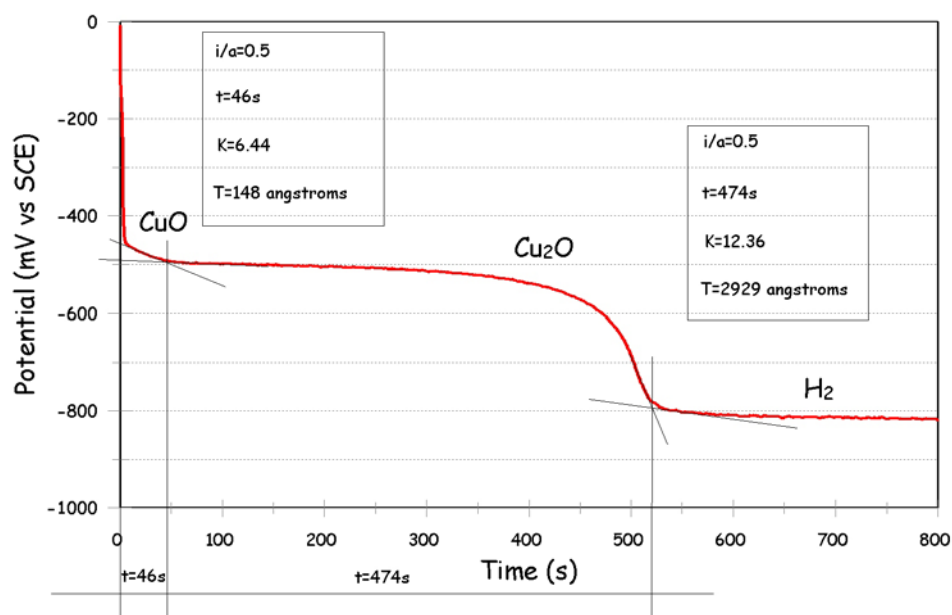


Figure 12:

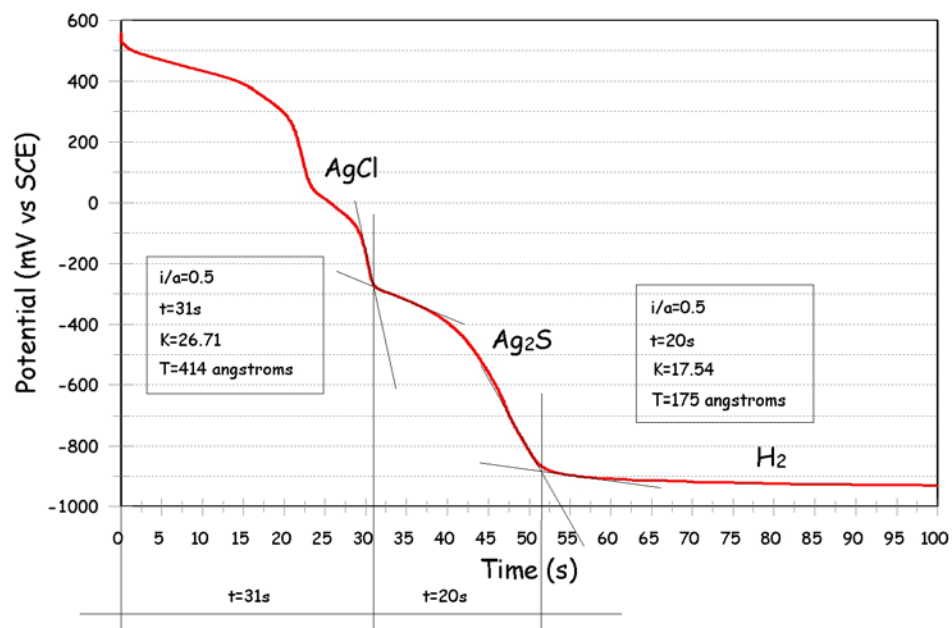


Figure 13:

Figures 12-13: The typical coulometric/cathodic reduction plots show how reduction times were extrapolated from inflection points of plateaus for different corrosion product species. The coulometric reduction current density used for this outdoor environment was $0.5\text{mA}/\text{cm}^2$. The total film thickness measured for copper by use of the coulometric/cathodic reduction technique was 3077\AA (148\AA for CuO and 2929\AA for Cu_2O). The severity level ranking of air pollutants was classified as GX (severe). The total film thickness measured for silver by use of the coulometric/cathodic reduction technique was 589\AA (414\AA for AgCl and 175\AA for Ag_2S). The severity level ranking of air pollutants was classified as G2 (moderate).

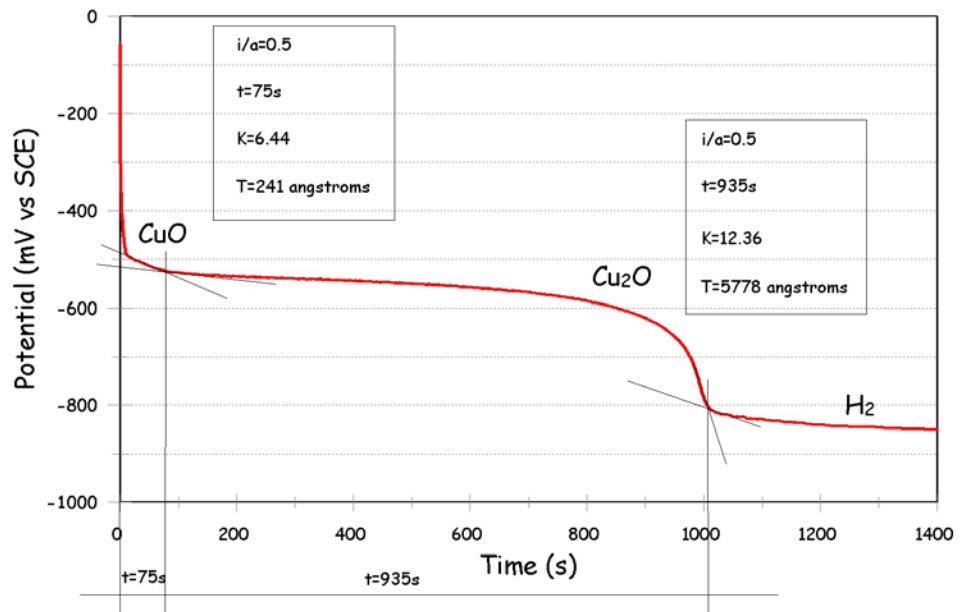


Figure 14:

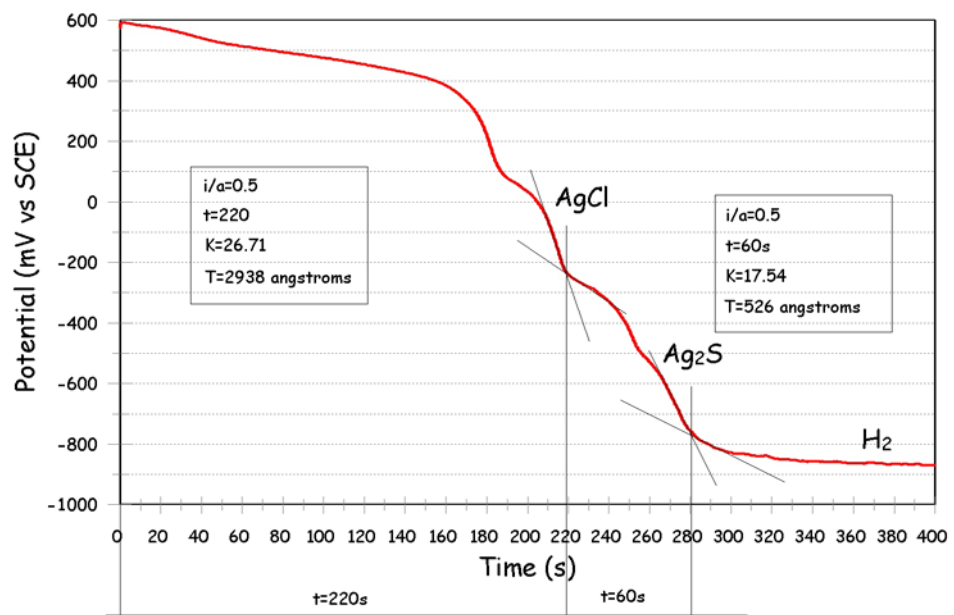


Figure 15:

Figures 14-15: The typical coulometric/cathodic reduction plots show how reduction times were extrapolated from inflection points of plateaus for different corrosion product species. Air pollutants detected in this outdoor environment were rich in mainly oxides, chlorides and sulphides. The coulometric reduction current density used for this outdoor environment was $0.5\text{mA}/\text{cm}^2$. The total film thickness measured for copper by use of the coulometric/cathodic reduction technique was 6019\AA (241\AA for CuO and 5778\AA for Cu_2O). The total film thickness measured for silver by use of the coulometric/cathodic reduction technique was 3464\AA (2938\AA for AgCl and 526\AA for Ag_2S). The severity level ranking of air pollutants was classified as GX (severe).