intertek capcis

Corrosion Controlled. Materials Assured.

# WORLD CORROSION DAY 2024

April 24th 2024

Hosted by

Tim Walsh

Professor Stuart Lyon

intertek capcis &

MANCHESTER 1824

The University of Manchester

# "CORROSION AND PROTECTION CENTRE INDUSTRIAL SERVICE"

- CAPCIS (Corrosion And Protection Centre Industrial Services) was originally formed at the University of Manchester in 1973 after the university was designated by the Government as the 'National Technical Centre of Excellence for Corrosion'
- Intertek, a FTSE 100 business acquired CAPCIS in 2007 providing CAPCIS access to a globally significant network of resources
- Intertek CAPCIS is a world leading authority offering independent 3rd party testing and consultancy services
- Intertek CAPCIS employs over 70 scientists, consultants and technicians who provide valuable support to help protect industrial assets worldwide
- Intertek CAPCIS is extremely proud of its long-term link to the University of Manchester and the fact that our connection is still strong after over 50 years of successful collaboration is testament to the strength and depth of that relationship

# "CORROSION@MANCHESTER"

1957: Corrosion research group formed in Chemical Engineering by Ken Ross

*First PhD awarded 1960: "The electrochemical behaviour of sprayed metals": Webster, P.H.N.*

1961: Corrosion Science Division of Chemical Engineering formed and Graham Wood hired

*1st cohort of the new MSc programme in Corrosion Science (still running)*

1969: Committee on "Corrosion and its Prevention" established by UK government

*Chaired by T.P. Hoar with Ken Ross as member*

1971: The "Hoar Report" on the Cost of Corrosion in the UK published its findings

*Recommendations included an industry advisory service and expansion of university teaching*

1972: Corrosion and Protection Centre established at Manchester (UMIST)

*Graham Wood, UK's first Professor of Corrosion Science ("Professor of Rust" according to Daily Mail)*

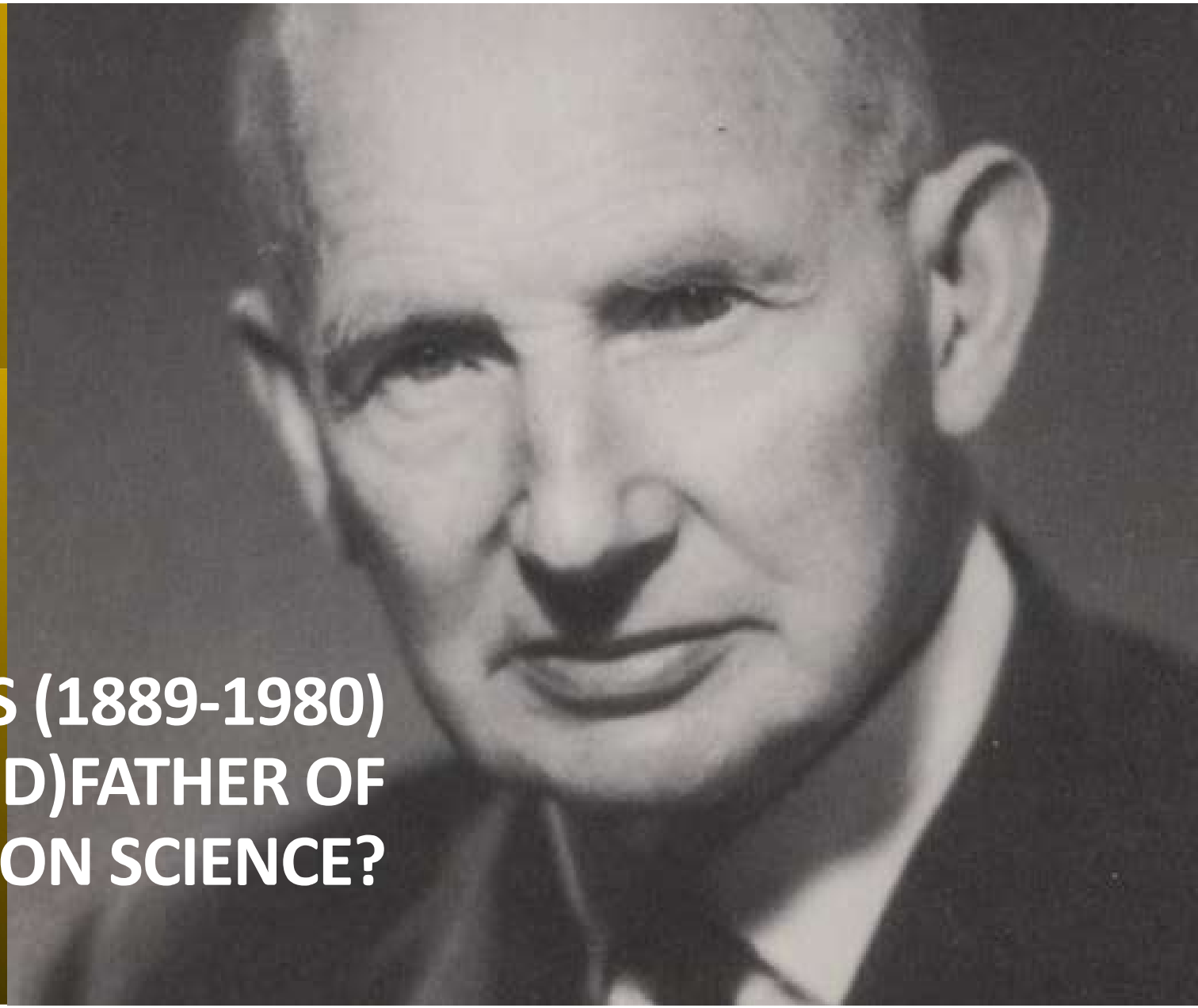
1973: CAPCIS established with UK government pump-priming

*Close academic links for > 50 years; the first job for many former Manchester students*

Ken Ross

Graham Wood

100 years of Evans



# ULICK EVANS (1889-1980) THE (GOD)FATHER OF CORROSION SCIENCE?

200 years of Davy

# HUMPHREY DAVY (1778-1829) THE (GOD)FATHER OF CATHODIC PROTECTION?

# ULICK RICHARDSON EVANS – THINGS YOU MIGHT NOT KNOW

- Ulick is the Anglicised version of the Irish name “Uilleag”; his father was Irish and was born in Cork
- He was the 5th out of 7 siblings with 6 sisters and no brothers; he never had any desire to marry.
- Evans was fluent in German and French and was familiar with several other languages
- He started working at Cambridge in 1921 supported by legacies from his maternal uncle, John Feeney, the former proprietor of the Birmingham Post. The Feeney charitable trust still exists to this day.
- He was a cross-country runner, rock climber and regular all-weather swimmer in the Cam
- He was awarded a DSc in 1932 and was thereafter known as “The Doctor”; he never studied for a PhD
- He got his first permanent position in Cambridge as “Assistant Director of Research” at the age of 45
- He was passionate against contemporary opinion that “*corrosion is a dirty subject meriting little attention*”
- His will provided a legacy for the establishment of a research fund to continue the study of corrosion: “*in Cambridge or in Manchester*”

**Manchester (U.M.I.S.T.) never saw a penny!**

# "THE CORROSION OF METALS", U.R. EVANS, PUB. 1924

Evans wrote the first comprehensive text book on corrosion; published some 100 years ago, it was not universally welcomed.

- "… the author, by seeking to tie everything down to an electrochemical explanation to the exclusion of all others, is taking too narrow a view …"
- "The problems of corrosion are so vast and intricate that it is impossible to deal adequately with them within the confines of some 200 pages."

*J. Newton Friend reviewed in Chemistry and Industry, Nov. 1924*

- In 1924 the electrochemical theory was still not fully accepted and arguments raged in the literature for years afterwards.
- His *magnum opus* "Corrosion and Oxidation of Metals" published at the age of 71 in 1960, was over 1000 pages long; supplementary volumes appeared in 1968 and 1976 totalling more than 500 additional pages


"The corrosion of metals" first edition cover

# CORROSION IN ANTIQUITY

Dehli pillar 2006


Corrosion damage “ferrum corrumpitur” must have been known in antiquity however the first written record is probably from Pliny the Elder in his Natural History, Book XXXIV.

*“Iron that has been heated by fire is spoiled unless it is hardened by blows of the hammer. It is not suitable for hammering while it is red hot, nor before it begins to turn pale. If vinegar or alum is sprinkled on it, it assumes the appearance of copper. It can be protected from rust by means of lead acetate, gypsum and vegetable pitch; rust is called by the Greeks ‘antipathia,’ ‘natural opposite’ to iron.”*

Pliny also provides the first mention of corrosion protection. We now know:

- lead salts can inhibit rusting, gypsum releases calcium ions (a cathodic inhibitor), while pitch potentially provides leachable organic inhibitors and a physical barrier

The “Dehli pillar is, of course, not “uncorroded”, rather we can see an oxide heat tint at the top and thin brown rust at the base where it is accessible. The dry, unpolluted environment and the low sulfur content of the iron explains its longevity.

# PHENOMENOLOGY

Robert Boyle: 1627-91
Wikimedia commons

- 1675: Robert Boyle published “Experiments and Notes upon the Mechanical Origin or Production of Corrosiveness or Corrosibility”
- 1788: William Austin (1754-93), physician and chemistry professor at Oxford, reported that water became alkaline “when it acts on iron”
- 1790: James Keir, a Scottish industrialist and amateur chemist, observed passivity when he reported to the Royal Society that iron ceased to react in strong nitric acid
- However, these were phenomenological observations only – no mechanisms were proposed.

James Keir: 1735-1820
Wikimedia commons

# EARLY FINDINGS (LATER IGNORED)

Charles Gaspard de la Rive (1770-1834)
Wikimedia commons

- 1819: Thénard, Professor of Chemistry at the École Polytechnique in Paris and discoverer of hydrogen peroxide, suggested that corrosion might be an electrochemical phenomenon
- 1830: de la Rive, Professor of Chemistry in Geneva, attributed the fact that acid attacks impure zinc more rapidly than relatively pure zinc to an electrical effect set up between it and the impurities present
- This was the first suggestion that material microstructure could influence corrosion

Louis-Jacques Thénard (1777-1857)
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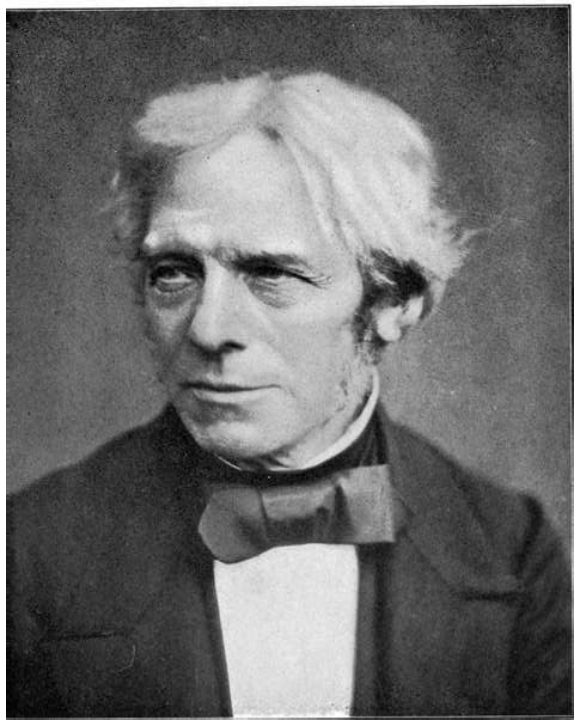
# ELECTROLYSIS AND PASSIVITY

Christian Friedrich Schönbein: 1799-1868
Wikimedia commons

- 1834-40: Faraday developed the essential relationships between chemical action and electrical current: Faraday's Laws
- 1836: Faraday and Schönbein corresponded regularly between 1836 and 1862 on the reason for Keir's observations
- While Schönbein thought that the metal itself was changed Faraday, presciently, proposed the formation of an invisible, protective layer such as an oxide



Michael Faraday : 1791-1867
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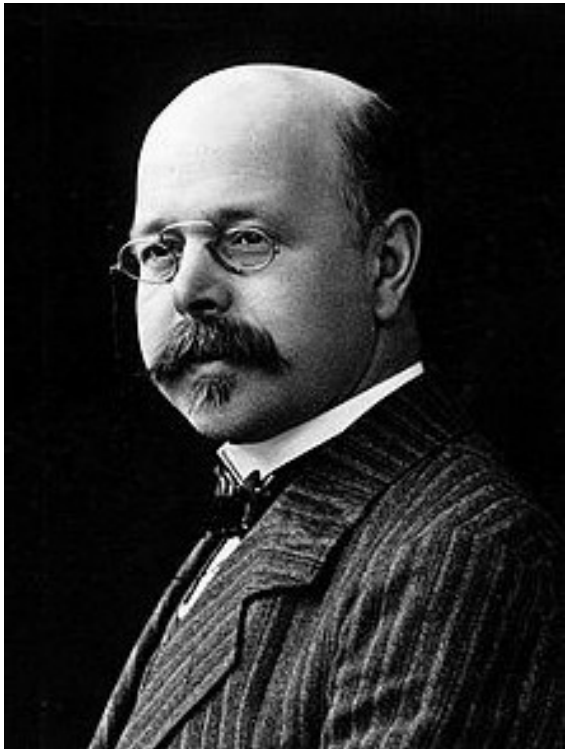
# ELECTRODE POTENTIALS

Wilhelm Ostwald: 1853-1932
Wikimedia commons

- Faraday's work on the Laws of Electrolysis were clearly applicable to corrosion processes but the link was evidently not made for two key reasons:
- Experimental measurement was not easy with the equipment of the day
- Theoretical understanding had to wait until the concept of potential was developed by Nernst and Ostwald during the 1890-1900s.



Walter Hermann Nernst: 1884-1941
Wikimedia commons

# “AGENTS OF CORROSION” - THE ACID HYPOTHESIS

Frederick Crace Calvert (1819-73)
Wikimedia commons

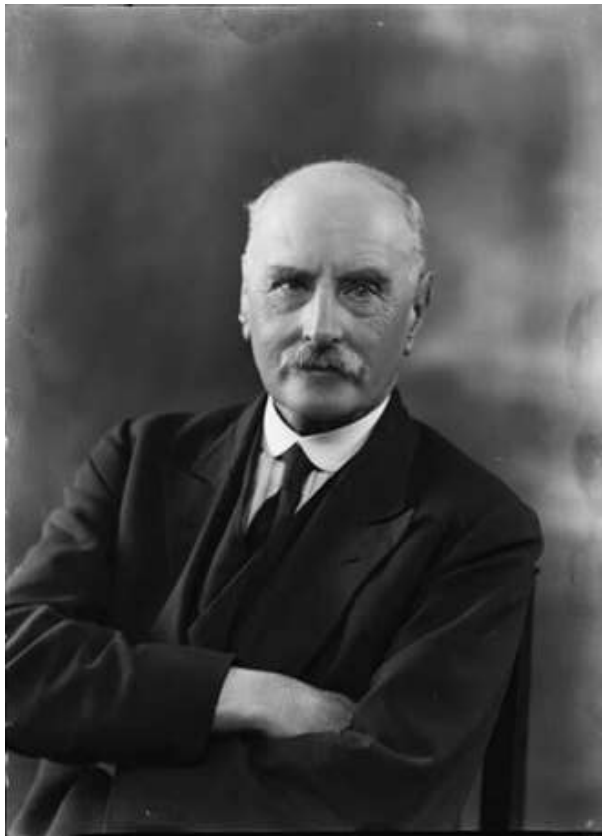
- After Faraday it was generally believed that corrosion was caused by particular chemical agents, particularly acids.
- 1871: Calvert believed that when he excluded carbonic acid from the environment iron did not corrode in water and oxygen alone
- 1888: Brown developed a chemical reaction mechanism describing this idea:

$$4(Fe + H_2O + CO_2) = 4FeCO_3 + 4H_2$$
$$4FeCO_3 + 6H_2O + O_2 = 2Fe_2(OH)_6 + 4CO_2$$

- This “explained” the observation that iron did not corrode in alkaline solution because it prevented rusting by absorbing carbonic acid.

Alexander Crum Brown: 1838-1922
Wikimedia commons

# "AGENTS OF CORROSION" - THE PEROXIDE HYPOTHESIS



Wyndham Rowland Dunstan (1861-1941 )
© National Portrait Gallery

- 1898: Dunstan, Professor of Chemistry at the Imperial Institute, repeated the work of Calvert and determined that corrosion of iron can indeed occur in the absence of $CO_2$ and that Calvert had not properly excluded carbon dioxide from his apparatus
- It had long been known that hydrogen peroxide was formed during certain physiological processes and also (from results by Schönbein) during the corrosion of zinc
- Dunstan therefore proposed that the production of $H_2O_2$, formed as an intermediate during rusting, caused corrosion.

$$Fe + O_2 + H_2O = FeO + H_2O_2$$
$$2FeO + H_2O_2 = 2FeOOH$$

- He explained the inhibitory ability of alkalis, chromates, nitrites on their "*power to decompose peroxide*"

# THE ELECTROCHEMICAL HYPOTHESIS

Willis Rodney Whitney (1868-1958)
Wikimedia Commons

- 1903: Whitney's paper "The Corrosion of Iron" was the first to apply Nernst's ideas on electrode potential to the processes of corrosion.
- *"Practically the only factor that limits the life of iron is oxidation, under which are included all processes whereby the iron is corroded, eaten away or rusted.*
- *In undergoing this change the iron always passes through or into a state of solution and, as we have no evidence of iron going into aqueous solution except in the form of ions (probably electrically charged atoms), we have really to consider the effects of conditions upon the potential difference between iron and its surroundings*
- *The whole subject of corrosion of iron is therefore an electrochemical one and the rate of corrosion is simply a function of electromotive force and resistance of circuit.*
- *If we now apply Nernst's conception of the source of electromotive force between a metal and solution we must conclude that the measured potential difference … equates to a force equivalent to 10,000s of atmospheres' pressure at ordinary temperatures."*
- These statements were hugely ahead of his time

# OXYGEN AS CATHODIC DEPOLARISER

William Hultz Walker: 1869-1934
© Science History Institute

- 1907: Walker, Cederholm and Bent first used ferroxyl indicator to demonstrate anodic and cathodic areas
- *"…the primary function of oxygen … is to depolarise those cathodic portions of iron"*
- *"… the rapidity of corrosion in water is a linear function of the partial pressure of oxygen"*
- *"… areas having a marked difference in potential exist … upon the surface of a piece of iron prone to corrosion"*
- 1908: Tilden also demonstrated the importance of oxygen in corrosion
- Both papers rebutted the acid and peroxide theories of corrosion, which nevertheless were still widely believed

William Augustus Tilden: 1842-1926
Wikimedia commons

# CONCENTRATION CELLS

Emil Warburg, 1846-1931
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- 1889: Warburg reported that an electric current could be generated between two metals with different concentrations of oxygen.
- 1916: Aston showed the role of local differences in oxygen concentration in the rusting of iron
- 1922: McKay demonstrated currents on a single metal surface could be generated by variation in local metal ion concentration
- These experiments demonstrated that galvanic corrosion did not require two metals of different composition but could be generated simply by local chemical differences

Robert McKay: 1887-1963
© The Electrochemical Society

# COST OF CORROSION

Robert Hadfield,
© National Portrait Gallery

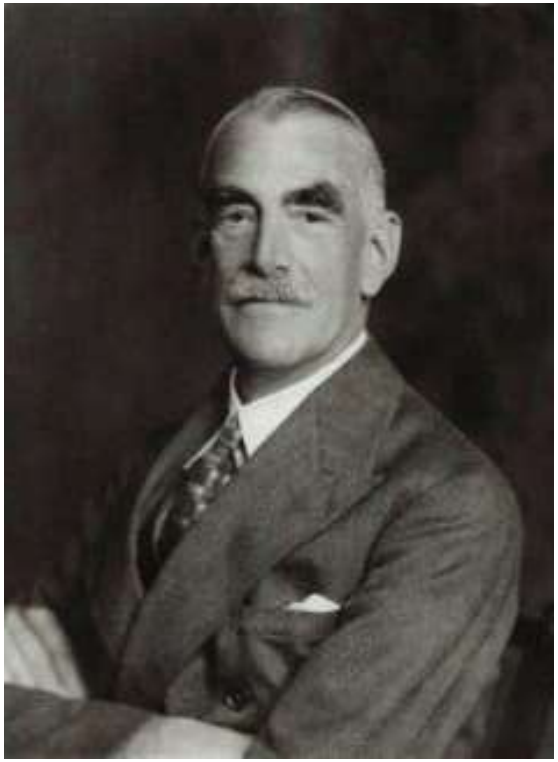
- 1907: “The Rusting of Iron”, W.A. Davis, Imperial Institute:
- LNWR rails lose 18 tons of steel daily: ~£40,000 pa (or £6.2m today)
- Annual cost of painting the Forth Bridge: 28 painters £1,700, paint £400; total £2,100 (or £325,000 today)

- 1922: “The corrosion of iron and steel”, Robert Hadfield
- Global estimated loss of steel due to corrosion 40,000,000 tons
- Cost of replacement and protection > £500 m annually (£77bn today)

- *“The introduction of alloy steels which possess higher capacity for resisting corrosion should be encouraged, and although higher in the first cost they will probably be found more economical in the long run.”*

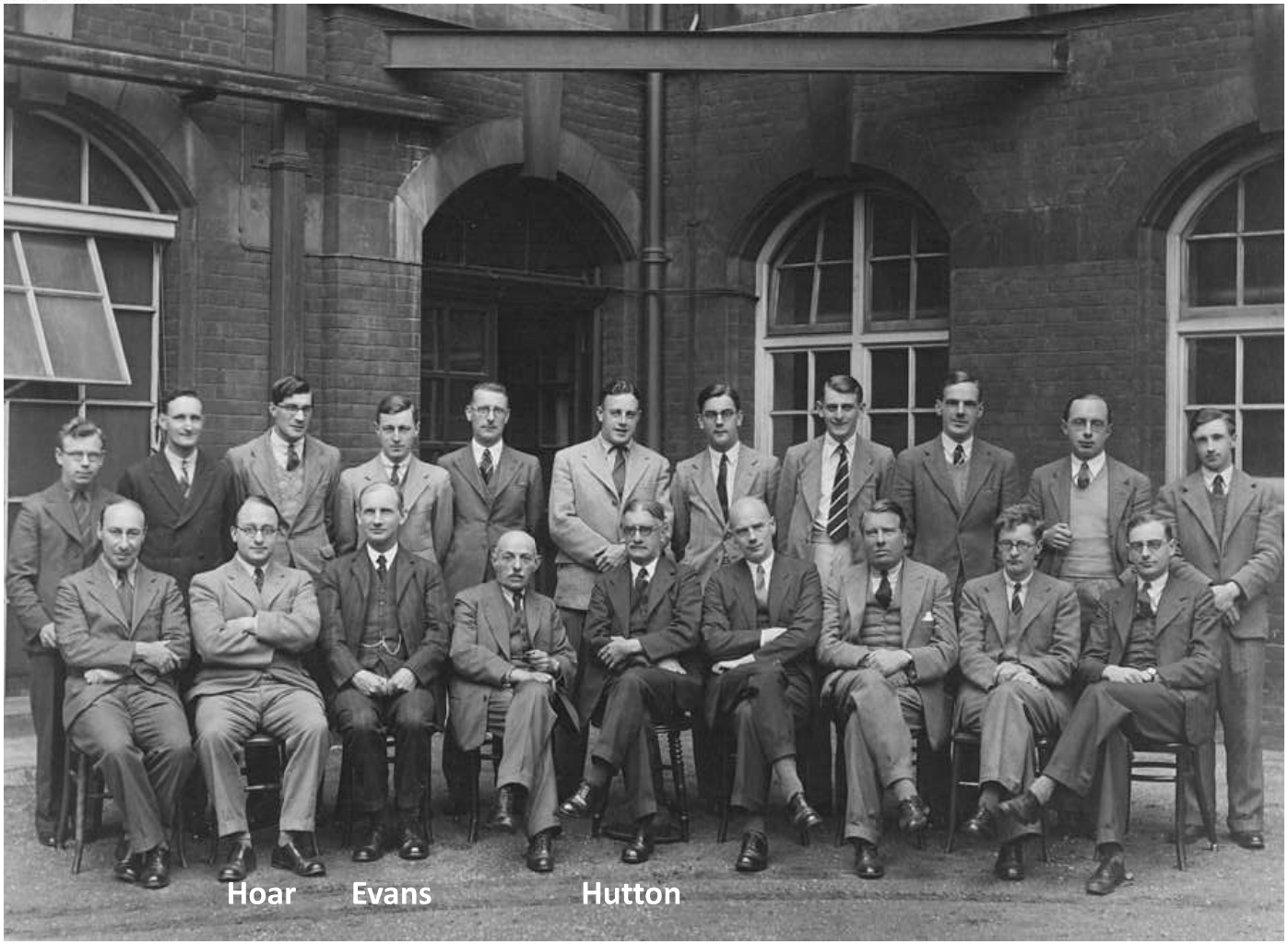
# SOME CONTRIBUTIONS

- Evans did not propose the electrochemical theory of corrosion but was a lifelong advocate for it and provided its solid experimental support.
- He worked with Bengough and the British Non-Ferrous Metals Research Association to devise principles for standardisation of corrosion testing
- He and Bengough were at odds for many years but eventually made a joint declaration in 1938 stating what matters they agreed on
- Evans devised simple benchtop experiments to examine hypotheses and did not just try to explain experimental observations
- Evans advocated the use of the ferroxyl indicator to visualise anodes and cathodes on corroding surfaces although he was not the first to use it.
- With Hoar he used constant current methods to determine polarisation curves and devised his eponymous diagrams to explain the processes occurring.
- He was the first to devise a method to selectively dissolve metals but retain any oxide thus isolating the films that formed on surfaces
- **Ultimately created the conditions that promoted corrosion teaching and research at Manchester (U.M.I.S.T.), and the establishment of CAPCIS, some 50 years ago**



Guy Dunstan Bengough: 1876-1945

# CAMBRIDGE DEPARTMENT OF METALLURGY - 1939






- T.P. (Sam) Hoar was Evans' PhD student
- Robert Hutton was Goldsmith's Professor of Metallurgy, previously Lecturer in Electro-Metallurgy at the Victoria University of Manchester
- John Agar the electrochemist joined Evans' lab in 1938 and so is also somewhere in this picture

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*Did you know: According to a NACE impact report it is estimated that corrosion costs the global economy $2.5tn USD per annum (equivalent 3.4% GDP)*

Intertek CAPCIS provides a broad range of services:

- Testing (Materials and Chemicals)

  e.g. Fatigue testing, Sour service, Inhibitor Chemical, Non-Metallics, Production Chemistry
- Consultancy Services

  e.g. Corrosion Risk Assessments, Materials Selection, Stray Current, Risk Based Inspection
- Failure Investigation

  Including – Root Cause Analysis, Expert Witness Services

**Please do not hesitate to contact us for any advice or support**



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# Watch This Space

Intertek CAPCIS will soon be launching a series of webinars that will focus on specific corrosion areas.
These webinars will be hosted by subject matter experts who will provide an in-depth overview of their specific area of interest.

Some of the topics we will be covering will include:

- Reservoir Souring
- Fatigue Testing
- Sour Service
- Corrosion Inhibitor Testing
- Cathodic Protection
- Asset Integrity Management

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