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Evolution of the role of Electrochemistry in Corrosion Engineering

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Abstract

Electrochemistry is not a primary science, since electricity is a corollary of both chemistry and physics, through thermodynamics and kinetics. Its impact in technology, and in chemical engineering too, is limited to special restricted areas, like electrodeposition, energy storage (with the well known and critical limitations), chlor-soda industry and some electrometallurgy (copper, aluminium...), while there is a wide use of electrochemical devices.

Provided that corrosion engineering be, outside US, a real profession, corrosion scientists are actually the main copy-writers of electrochemical methods in corrosion research in the laboratory (see, e.g. the proceedings of AETOC workshops) while anticorrosion technologists tend to trust physical and/or mechanical methods both for testing and for monitoring, as well as for forecasting reliability and expectancy of useful service life of structures.

Moreover, also in failure analysis often physical, chemical, mechanical test methods are used (SEM, TEM, EDAX, ...) instead of electrochemical ones. International Standards concerning electrochemical testing and monitoring methods are rare, and some of them since long time remained in form of Draft (ISO 16773 1 -4 - 2007-2009).

In this paper we review the evolution of electrochemical methods in corrosion research and we describe some examples of the few instances when electrochemistry is usefully employed in corrosion control on site:

1) corrosion control of steel pipelines through Rp monitoring
2) radio-monitored electrochemical noise on US Navy ships
3) EIS monitoring on steel bridges
4) EIS monitoring of structures underwater

5) Rebar corrosion monitoring on concrete viaducts

Keywords: electrochemistry, history, education, corrosion engineering

Introduction

The history of chemistry may be said to begin with the distinction of chemistry from alchemy worked out by Robert Boyle (1627-1691) in his work The Skeptical Chymist (1661). Both alchemy and chemistry are concerned with the nature of matter and its transformations but, in contrast with alchemists, chemists applied the scientific method.

The action of a chemist can be divided into categories based on *making something happen* and *characterizing what happened*. In this latter field, Antoine-Laurent de Lavoisier (1743 - 1794), profiting of both his wide skills and of many others' discoveries, gave rise to modern chemistry…a demonstration that intelligence is the art of acknowledging the relationship between different events.

Modern science was, at the beginning, totally interdisciplinary, even building new disciplines, like physical chemistry and, actually, electrochemistry. The connecting tissue was, no doubt, the Enlightenment, the Acadaemia, the laical approach to knowledge, lost - unwillingly - since from the Hellenistic times. Our Colleagues of CERN say: science is either physics or stamp collection. In answer, we might oppose that Physical Chemistry is everything that is interesting. And electrochemistry? The accumulation of "charges" on selected materials was acknowledged with wonder by Thales (600b.C), Theophrastus from Ephesus (900b.C.), and later Plato (428-348b.C), not forgetting Pliny the Elder (23-79), who, by the way, was not convinced of the metaphysic reasons why "ferrum corrumpitur". It was only in the sixteenth century that electricity began to be understood. William Gilbert (1544-1603), was among the first to experiment with electricity and magnetism. The first generator of static electricity by friction between a large sulfur ball and a pad was constructed by Otto von Guericke (1602-1686) in 1663. In 1781 Charles-Augustin de Coulomb (1736-1806) propounded the law of electrostatic attraction. Benjamin Franklin (1706-1790) might be considered responsible for the concept of flux, as precursor of the concepts of electromagnetism developed by Andrè Mariè Ampère (1775 - 1836).

We might consider Luigi Galvani (1737-1798) as the ancestor of bio-electrochemistry, a discipline to-day at the top of applied research as for neuronics, bio-sensors, bio-robotics. Adding the concept of "nano" to the one of "mechanics", through the application of advanced electrochemistry, a new branch of electro-chemo-mechanic-engineering is widespreading: neurorobotics. The long time struggle to accumulate electricity, leading practically only to the Leyden jar produced by Pieter van Musschenbroek of Leiden (1745-1746), was won by

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Alessandro Volta (1745-1827). He won a battle, but the war to achieve a safe, efficient, reversible, scaled-up accumulation of electrical power is still now-a-days fought with scarce success. On the other hand, it was Volta who, through the innovation caused by the appearance of two gases from one liquid, the electrolysis of water, opened the way to the quantitative laws of Michael Faraday (1791 - 1867) and to industrial electrochemistry.

Electrochemistry and Technology

Electrochemistry is a subsidiary science, needing the application of the laws and equations pertaining to chemistry, physics, thermodynamics, kinetics, fluid-dynamics, mechanics, and hence to the original definitions of heat, flow, energy, entropy, reaction rate...The approach to learning as well as to using the tools of electrochemistry is therefore not immediate and needs a global vision of both the fundaments and of the widespread implications in so many branches of phenomena. Including the knowledge that love is mainly the effect of some bio-electrochemical reactions (better to forget it). In the field of corrosion engineering as well as of electrodeposition technology electrochemistry might be seen as easier and more attractive if, while teaching the basics, it was made clear that all those theories and laws concerning the carrying and the transfer of charges meet in practice a lot of approximations, exceptions, deviations facing with rough, wild, not friendly surfaces. Therefore, some main concepts should be kept in mind in sharing the knowledge of electrochemical phenomena in the frame of the teaching of electrochemistry in the Courses of Engineering and of Materials Technology:

1) The relative weight of fundamental laws and practical applications. Actually the electrochemical processes may involve transport of ions within a single phase, allowing electrical conductivity; on such subject the teaching concerns: ionic activity, Debye-Huckel theory, ionic strength, mobility... I'd like to compare the long dissertations on such concepts to the knowledge of the internal combustion engine as related to car driving. Electrochemistry of interphases needs a quite different, less detailed approach, focused on applications and achievements,
2) A well defined concept of reversibility and irreversibility. Most electrochemical processes involve transport of ions or electrons across phase boundaries, resulting in interfacial potential difference (a few notes are needed on electrical double layer) and hence in electron-transfer reactions which, carried out at anode and cathode, are at the basis of electrochemical engineering. Here, a peculiar bi-polar aspect of this technology appears:
   a) the utopical trend towards reversibility in all those processes aimed to "production" (electrochemical power sources, chlor-alkali industry, metal extraction...), has developed technological approaches towards reversible

reactions limited mainly by economical restrictions, but thermodynamically conceivable, even if kinetically not realistic. See, e.g. the many innovations available in the composition of Dimensionally Stable Anodes for the Chlor-Alkali production and never passed from the Laboratory to the industrial scale [1].

b) the struggle, never won, of corrosion engineers against the spontaneous, reverse reaction of metals towards the original ores, from which they were extracted by metallurgical processes; it follows that anticorrosion technology is not necessarily an electrochemical one; actually, a spontaneous electrochemical process like corrosion has to be fought not necessarily with electrochemical methods. Instead, the corrosion mechanisms, that are strictly electrochemical in nature and that were the object of wide and successful both scientific and technological studies in the last sixty years, are, on the contrary, scarcely the object of both high and basic education. It means: know well your enemy and then fight him with any kind of weapon. We'll develop these concepts in the following.

3) It is important to stress the peculiar aspects of the multiphase electrochemical reactions, subjected to a myriad of parameters, not all of them suitable to be controlled, modellized, expressed by equations. Even if one of the best qualities of electrochemical processes is their relative easiness to be scaled-up from the laboratory experiments, in many instances it is important to follow the approach of "how" they work rather the impervious path of "why". It is the case, e.g., of electrodeposition, electro-erosion, cathodic protection of off-shore platforms, even fuel-cells, whose scientific evolution was proceeded by empiric approach, given their urgent need for space exploration.

A tale of electrochemical engineering

A young research fellow of the Karpov Research Institute of Moscow in the late thirties of last century published a paper about electrochemical production of pure Manganese in laboratory. One night, at the beginning of WW2 a loud knocking at his door announced a visit of KGB. As easily understandable, his frightened thoughts went to gulags, (and hided all his roubles in an internal pocket of his overcoat...) but, instead, after long dedalic detours on a big black car he found himself in front of Stalin, surrounded, at 3a.m, by the whole Politburo.

- Are you Raphael, the son of Elia Agladze, my childhood's Georgian friend?
- I am
- Are you able to produce Manganese?
- I got some grams
- I need tons in two months
- but...
- With this paper and my signature you can get all means you need.

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Raphael went to Georgia (where, beside wineries, rich Manganese ore mines exist), got all huge grape step-on barrels he could find to build electrochemical cells, got power sources by flights from the trans-Uralian factories and produced the first tons of pure Mn by which the ballistic steel for USSR tanks and hence the tanks themselves were made available. Stalin, actually, had not been caring of the advice of his intelligence about the need of such metal before. Raphael Agladze (1911-1989) got the Stalin Prize, became Academician, first of USSR and then of Georgia. A great Scientist, a great Technologist, He was the founder and the director (1956-60) of the Institute of Applied Chemistry and Electrochemistry (at present Raphael Agladze Inorganic Chemistry and Electrochemistry). He rests in Didube Pantheon. One of the least known of the very many adventures of electrochemical engineering.

Evolution of the role of Electrochemistry in Corrosion Engineering

Since long time ago both NACE and EFC have been stressing the urgent need to widespread the basic knowledge of both electrochemical corrosion mechanisms [2], and of the main anticorrosion procedures as the outstanding tools to cut-off the unbearable costs of the advanced degradation of both artifacts, plants and structures. Very seldom now-a-days the reasons for the met damages are unknown: very frequent is instead the discovery of a trivial mistake in the choice of compatibility, assembling, applied loads, protecting coatings, all the mistakes connected with the scarce acquaintance with both electrochemistry and corrosion control technology. During EUROCORR 1997, as the President of EFC, PLB asserted:

"I am far from saying that fundamental corrosion research is obsolete; but a corrosion scientist today is asked to remember that corrosion is a practical problem, an economic waste as well as a cultural and technical nonsense even for those people, too many of them, who actually deal with critical operations related to durability and reliability; but they just ignore and hence don't care.

"A corrosion scientist, involved in his sacred and inviolable researches aimed to approach the ... virtual world, should remember that by solving many practical every-day problems an innovation, an advancement of science, a good publication may come; in the meantime, it is coherent with the priority needs of our field of interest that are, between others: - education, continuing education at all levels of people involved; this is the most important item, since it is necessary to spread out knowledge of the very simple corrosion principles in order to avoid the most elementary mistakes!"

A deeper interaction should be active between pure and applied science, or better between Science and Engineering.

According to the official definition of Science and of Engineering “Science is knowledge based on observed facts and tested truths arranged in an orderly system that can be validated and communicated to other people. Engineering is the creative application of scientific principles used to plan, build, direct, guide, manage, or work on systems to maintain and improve our daily lives"

A recent paper [3] aimed to improve durability and reduce maintenance costs of battle ships, enhancing the awareness of Navy sailors about the corrosion problem on a ship, training them in the use of multimeters to assess the outcome of bimetallic corrosion. Here is the aim as it is expressed in the paper:

"Since a ship may be at sea for a long time, it only makes sense that the crew should have the knowledge and ability to fix corrosion problems within their scope and be able to perform a self-assessment on the success of their work. A deployed unit is very expensive and time consuming to support. Armed with the right kind of tools and knowledge, survivability will increase, costs will drop, and the crew's morale will improve."

Had we an Award to deliver, Nichols would be the recipient! He is actually a corrosion engineer using electrochemical methods in corrosion research. As a frequent Participant in Corrosion and related Topics Conferences, it is our impression that corrosion scientists are actually the main copy-writers of electrochemical methods in corrosion research, using and developing them in the laboratory (see, e.g. the proceedings [4] of AETOC workshops) while anticorrosion technologists tend to trust physical and/or mechanical methods both for testing and for monitoring, as well as for forecasting reliability and expectancy of useful service life of structures.

Moreover, also in failure analysis often physical, chemical, mechanical test methods are used (SEM, TEM, EDAX, ...) instead of electrochemical ones. As a matter of fact, along with the years there was an increasing popularity of corrosion problems among science and technology, with corrosion mechanisms, passivating alloys, high-tech equipments, sophisticated test methods at the centre of interest, while scarce attention was deserved by corrosion science, among other anticorrosion technologies, to coatings, and more so to organic coatings, even if paints account for 50% of total corrosion costs. It looked like that, in general, paints were a black box for corrosionists while corrosion mechanisms (and electrochemistry) were the black box for anticorrosion technologists.

Many years had to pass before EIS became more than a "UFO" in the paint Industry, and many years before Coatings became an important item inside EFC. In '92, while the Coating Working Party (WP14) was conceived, still it was among many EFC Members a "wishy-washy" wishful thinking.

In 1993, PLB was appointed as the first chairman of WP14, which organised its first full day session at EUROCORR '94 in Bournemouth. In 1999, an international workshop on the 'Application of Electrochemical Techniques to Organic Coatings' was held at Schliffkopf in Germany and WP14 was also involved in the organisation of a session at ISE '99 in Pavia, Italy. In 1999, Dr J. Vogelsang succeeded to the chairmanship of WP14. As early as 1995, WP14 had turned its attention to the use of electrochemical impedance in the study of corrosion protection by organic coatings, and the new chairman soon formed a Task Group to develop a standard for Electrochemical Impedance Spectroscopy (EIS), which met at Stuttgart in March 2000 and decided to undertake a collaborative test programme,

This led subsequently to the establishment by Dr Vogelsang of a new working group of the International Organisation for Standardisation, ISO/TC 35/SC 9/WG 29: 'General test methods for paints and varnishes - Electrochemical methods', which met in Pittsburgh in June 2001 and agreed to develop a joint ISO/ASTM standard for the measurement of organic coatings by EIS. The first two parts of a multi-part international standard on Electrochemical Impedance Spectroscopy (EIS) of high-impedance coated samples (ISO 16773) have now reached the International Standard stage. In 2001, Prof. L. Fedrizzi (Italy) became the new chairman of WP14, which has since organised international workshops on 'Advanced Electrochemical Techniques Applied to Organic Coatings' (AETOC), the seventh edition of which was just held in Mons, Belgium, last April.

From the above we might extract the sensation that electrochemistry has been widely useful and source of smart evolution along with its application in corrosion science. Extremely sophisticated electrochemical test methods are made available and validated in quite reliable Laboratory experiments. But when it comes to application on-site, corrosion monitoring with the even simpler methods, quite optimised by long experience, like linear polarisation technique, are seldom found as required technique in designing plants or structures. The widest use is found in reinforced concrete where, by the way, the best results might be obtained with the embedded probes, while the external devices suffer from field effects and are less reliable. E.I.S. can also be applied on-site if only very few minor modifications in the rebars organisation might be designed during construction. It might hence be applicable on the structure the system (Fig. 1) which was successfully tested in the Laboratory and widely used to check the protecting properties of either modified mortars or organic protecting coatings on concrete [5]. An example of electrochemical monitoring on site, with the possibility of detecting possible corrosion as a function of depth of the embedded rebars is reported in a recent paper [6] as related, among others, to a Brenner Highway viaduct in Italy, where severe corrosion is viable due to the extended use of de-icing salts. An example of available sensors is shown in fig. 2

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Fig.1: Experimental set-up for monitoring rebars corrosion as a function of embedding mortar thickness

Fig.2: On-site sensor for monitoring rebars corrosion as a function of embedding mortar thickness (CorSenSys)

It is well known that in US a wide use is made of electrochemical devices for corrosion testing and monitoring on-line, nevertheless it is not easy to find in the open literature detailed examples of successful application of electrochemical testing on-site. In the authors' opinion, the detailed description of corrosion case-histories with report on causes, protecting procedures, international standards application, monitoring, etc., as related to bridges, pipelines, off-shore structures, harbours or whatsoever other artefact might be of utmost interest, and should not be considered of minor interest for the advancement of science. By the way,

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surgeons are often basing their professional curriculum on the publication of report of a successful, difficult surgery, and the advancement of science follows (and of life expectancy also...).

An interesting case of successful application on site of electrochemical test methods is reported by F.Mansfeld and co-workers [7] who collected electrochemical impedance and noise data for three coating systems applied on steel during exposure to natural seawater at Key West, Florida for 9 months. Potential and current noise data have been determined simultaneously by remote control via modem from CEEL. Analyses of the electrochemical noise data have been performed in the time and in the frequency domains. The mean potential Ecoupon and the mean coupling current Icoupon, between two coupled electrodes of the same material, the standard deviations of potential ·{ V(t)} and current noise ·{I(t)} fluctuations and the noise resistance Rn, obtained as the ratio of these two values have been calculated for each measurement which was carried out twice per week. An outline of the experimental set-up suitable to monitor the corrosion trend on-site from the Laboratory is shown in fig. 3.

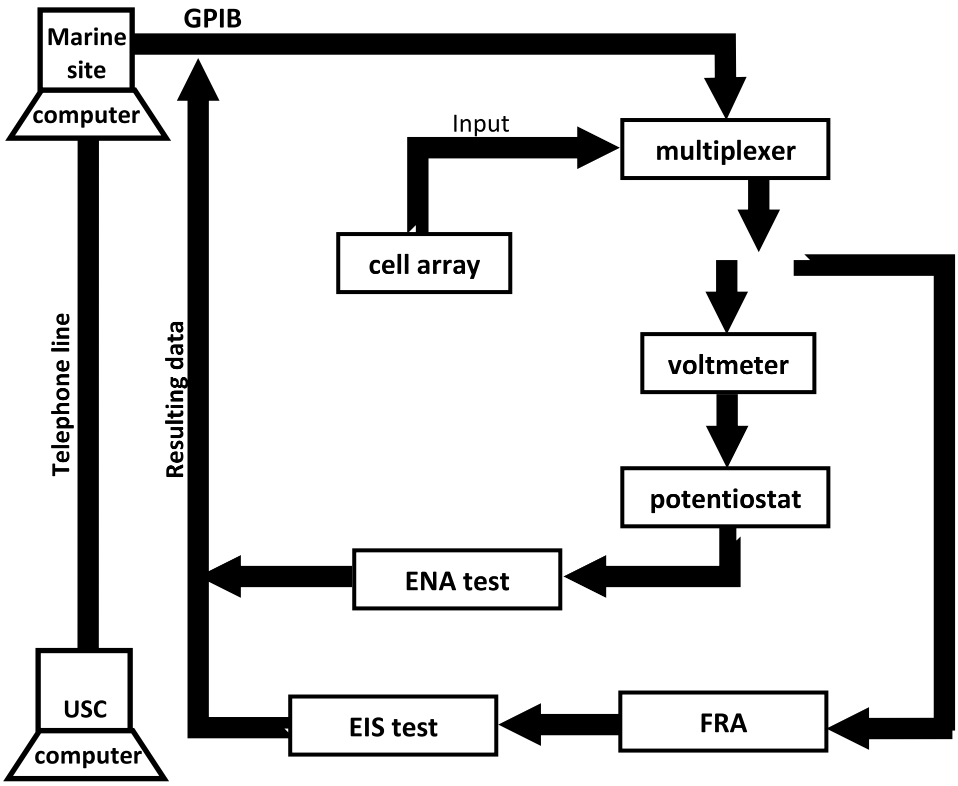

Fig.3: Experimental set-up suitable to monitor the corrosion trend on-site from the Laboratory[7]

This is an interesting case but, as far as we can know, it did not give rise to an adopted continuous profitable tool for corrosion engineering. Actually, since 1998 a comprehensive survey of the existing electrochemical test methods was published by Murray [8], with more than 240 references, and a more recent one by Song-I et alii [9] but very few instances are available of reports concerning “official” continuous electrochemical evaluation of corrosion on structures.

An interesting exception is provided in Europe by Poland, a huge, plain Nation rich of waters and hence of bridges, the highest part of which are coated steel constructions. Since many years the performances of coatings on bridges (and on other structures like electricity transmission towers) are monitored by on-site E.I.S. measurements [10]. The on site results correlated well with results obtained for the above mentioned coatings and linings in laboratory conditions. Measurements performed allowed to locate regions of especially high corrosion hazard on large structures and to compare the protective properties of different paint systems under actual exploitation conditions. Systematic impedance evaluation of coatings and linings could be used to predetermine their barrier properties and to forecast their durability in natural conditions. During the execution of anticorrosion works with the use of coatings, impedance investigations also could provide data attesting that a given criterion in quality control was respected and later allowed significantly earlier determination of their quality as compared to visual evaluation of damage to protective systems.

An evolution of this technology [11] was made available during the systematic testing of coatings suitable to protect steel barriers buried in the Venice lagoon in order to avoid water contamination from polluted soils. During underwater on site EIS measurements there are many technical problems with the insulation of electrical connections, the mounting and leak tightness of the measurement cell and the exclusion of measurement of electric capacitance between the counter electrode and surrounding constructions. These problems were successfully solved by the team of scientists from Road and Bridge Institute, Trento University and Atlas Sollich Electronic Systems Ltd.

Fig.4: Cell for underwater E.I.S. measurements [11]

Impedance spectroscopy performed on site for coating systems underwater or in splashed zones requires a specially prepared measurement cell (Fig. 4). The main features of the cell are:

- Very low electrical capacitance, software compensated,
- Easy mounting in underwater and above water conditions,
- Very high impedance of the cell construction materials,
- Very good insulation of electrical connections,
- Avoiding the measurement of electric capacitance between the counter electrode and surrounding constructions (obtained with a double walled cell).

An example of the E.I.S. spectra obtained on a submerged coating at different times of immersion is shown in fig. 5.

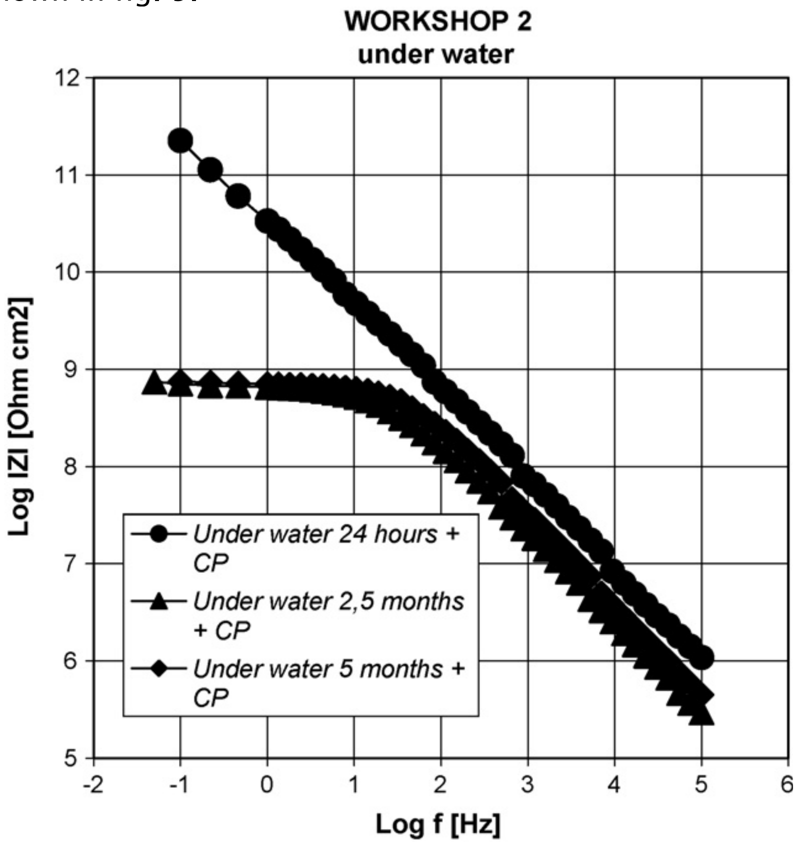

Fig. 5: Impedance modulus spectra of a coating system in underwater conditions.

Conclusions

Electrochemistry is the driving force of almost all corrosion mechanisms. Corrosion science has, during the last sixty years, accomplished the task to explain practically all the features of the spontaneous environmental degradation of metallic and even semiconducting materials; all possible countermeasures have been widely explored and validated. Nevertheless, awareness of corrosion danger as well as of its enormous economical, social, environmental fall-out is still the privilege of a few.

In a multidisciplinary world of technology, electrochemistry is the driving science of many advanced Laboratory experiments, while the electrochemical approach to corrosion engineering is not common. One possible reason is possibly found in the way electrochemistry is taught, featured as a fundamental theoretical science, subsidiary of physical chemistry, and not as a useful tool to investigate as well as to prevent and minimize corrosion problems.

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