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Detection of Corrosion Risk beside Patch Repairs

Detección del riesgo de corrosión al lado de las reparaciones por parcheo

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ABSTRACT

As a rule, in real concrete structures reinforcement corrosion generates cracks parallel to the steel but so randomly distributed that surface spalling is irregular. During inspection and subsequent patch-repair planning, the areas most intensely cracked are generally deemed to be an indication of greater corrosion. The unit for justifying the need for repair measures, in turn, is the area of the regions affected by cracking. Inasmuch as the area corroded is normally greater than the area affected by cracking, if only the latter is repaired damage may re-appear years or even months after intervention due to the existence of undetected steel corrosion. The amount of area in need of patch repair is a key issue with significant financial and safety implications. The mechanisms governing corrosion and the feasibility of galvanic coupling between repassivated and adjacent regions are discussed hereunder. The article also addresses the effect of using steel primers in repaired zones and bonding agents between the existing and repair materials. It likewise describes the three techniques that can be used to determine how much contaminated concrete should be removed: two types of chemical analysis (pH or chloride content) and corrosion parameter measurements (corrosion rate) in areas adjacent to the cracked or in the repaired zone.

KEYWORDS: Repair, corrosion, macro-couple, primers, linear polarization.

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RESUMEN

En general, la corrosión genera fisuras paralelas a las armaduras que aparecen aleatoriamente produciendo un saltado del recubrimiento irregular. Durante la inspección para definir el plan de reparación por parcheo las áreas más fisuradas se consideran como las más corroídas. A su vez, se toma como unidad de área a reparar la extensión de las áreas fisuradas. Sin embargo, como la extensión corroída es mayor que la fisurada, el daño reaparece en años posteriores. La cantidad de área a reparar es pues un aspecto que tiene implicaciones económicas y de seguridad. En el presente trabajo se discute la posibilidad de crear pares galvánicos entre las zonas reparadas y las adyacentes. El articulo también aborda el efecto del uso de imprimaciones de la armadura y el uso de "puentes de unión" entre el hormigón original y el material de reparación. También se describen las tres técnicas que se pueden utilizar para determinar cuánto hormigón contaminado debe retirarse: dos tipos de análisis químico (medida del pH o del contenido de cloruros) y medida de los parámetros de corrosión (velocidad de corrosion) en las áreas fisuradas o adyacentes a la zona reparada.

PALABRAS CLAVE: Reparaciones, corrosión, macropar, imprimaciones, polarización lineal.

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1. INTRODUCTION

With the gradual ageing of their constituent concrete, a growing number of buildings and infrastructures are deteriorating. Where structural concrete is involved, the most

 Persona de contacto / Corresponding author: Correo-e / email: candrade@cimne.upc.edu (María del Carmen Andrade) widespread type of damage is reinforcement corrosion, caused primarily by chlorides (in marine environments) or de-icing salt ingress or progressive carbonation of the concrete cover. When decay appears, it adopts the form of surface rusting or cracking parallel to the steel. If allowed to

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Figure 1. Stages in patch repair: a) inspection to detect damaged areas; b) removal of damaged concrete; c) reinforcement de-rusting and primer application; d) geometric restoration, and e) replacement of concrete cover.

go unrepaired, such damage may cause load bearing to dip below the design specifications.

As repair entails significant owner investment, its optimisation has financial implications, particularly where a whole building stock or several infrastructures are affected. Public authorities responsible for road, railway or harbour safety and operationality are faced with that situation.

So-called 'patch' repair, applied locally, consists in the measures listed below, the first of which is inspection to identify the areas in need of intervention (figure 1):

- a) identification of the damage and the zones to be repaired
- b) removal of the damaged concrete cover.
- c) de-rusting of the steel and (optional) application of a primer to enhance corrosion protection or strengthen the bond to the new material.
- d) (optional) application of a bonding agent between the concrete and new material and restoration of member geometry with the new material to replace the former cover.
- e) application of new cladding or paint to conceal the patchwork.

This operation is time- and labour-intensive for it entails careful workmanship to ensure the concrete will recover its functionality (good bond between new and former material) and to prevent cracking in any of the intermediate stages.

Experience has shown such repairs to be short-lived, however, even where workmanship is up to par [1]. A survey conducted under the European CONREPNET project [2] found that after 20 years only 5% of patches had never called for further repair. A number of causes were defined, including incorrect identification of the corroded areas or unsuitable choice or inadequate on-site placement of materials. The repair materials themselves were found to be durable, although their composition has changed extensively over time, given the constant improvements introduced by manufacturers.

One of the main reasons given for patching failure was that the area repaired was smaller than the area affected, for the area of the surface affected by rust stains or cracks is not necessarily indicative of where corrosion has set in. As the corroded region often extends beyond the area containing such external signs and as patching involves removal of the visibly deteriorated concrete cover, the adjacent areas at risk of corrosion may become depassivated in the wake of repair. In other words, a galvanic couple may form between the repaired zone, acting as a cathode, and the unrepaired zone, acting as an anode, which becomes depassivated. The primary concern around local or patch repair is therefore its mechanical and electro-chemical efficiency. Debate is ongoing on the effect of patch repair-induced galvanic coupling, with some authors [3-11] concerned that it hastens corrosion in the adjacent areas. Others [12-24], however, have shown the effect to vanish in the short term or to decline in the presence of steel primers. Consensus around the galvanic couple effect and its duration in actual structures or the use of primers on steel has proved elusive because the studies on the subject have been conducted under different climatic and laboratory conditions and with different types of specimens.

This article addresses that problematic issue, describing in the results and discussion what is deemed a 'galvanic couple'. possible corrosion rates and depassivation circumstances. It also summarises and analyses earlier findings [14-24] on galvanic couple measurement which simulated the use of different types of primers, chloride contents in the areas adjacent to the repaired zones and the effect of using a bonding agent between the new material and the existing concrete. A third section of the paper deals with the issue of how much to repair. Although the greater the amount of damaged concrete removed the more effective is the intervention, economic factors must also be weighed, and optimised and structural integrity compromised as little as possible. Given, then, that inspection must clearly identify the extent of the repair, the tests to determine the remaining carbonation or chloride content in the areas adjacent to the repaired zones, along with the use of electrochemical techniques for measuring corrosion, are also briefly analysed.

2. EXPERIMENTAL

The procedures analysed below were conducted either on purposely prepared laboratory specimens or on members in existing buildings tested in situ. The types of test pieces are described next, and test specific characteristics are specified in the respective sub-section of the results.

2.1. Samples used to study possible galvanic action

Macrocell action was explored with a variety of devices, sample types and existing structures. Only the procedures used to illustrate this article, the findings for which have been published elsewhere [14-24], are briefly described below.

- 1. *Diffusion cell-type* or double electrode devices (figure 2 left): diffusion cells, in which a closed vessel is divided into two chambers by a concrete disk, are ideal for studying galvanic effects because they ensure anode and cathode separation, use different electrolytes in each chamber, can be deaerated independently and deployed to test different types of concrete, sample thicknesses and so on [22,24].
- 2. Specimens with embedded electrodes [15,17, 21] also provide for the use of different conditions in each electrode (figure 2 right).
- 3. Beams or slabs with segmented rebar (figure 3): Using concrete, galvanic couple testing consists in making medium-sized specimens with at least one continuous and one segmented bar like the one shown by way of example in figure 3. The wires attached to the segments bear a connection electrically insulated (taped or resin-based) from the concrete to prevent the formation of galvanic couples between copper and steel. With segmentation, the galvanic current (I_g) with a zero-resistance ammeter (ZRA) [16,19,21,24] and corrosion rate (I_{corr}) through the Linear Polarization technique can be measured separately in each segment to assess the impact of the variables studied (such as humidity, temperature and chloride content) relative to overall unsegmented behaviour.

In all the cases ribbed bars were used. The specimen had two bars 60-cm-length placed in the bottom and two in the upper part as shown in the photo of figure 3. Those in the bottom and one in the upper zone were continuous. The other bar in the upper zone was segmented in seven parts that were elec-



Figure 2. Left: Diffusion cell to study galvanic couples; Right: Laboratory specimen to study galvanic couples.

trically connected. Each part of the segmented bar had 8 cm of exposure length and all of the reinforcing bars were 6 mm in diameter. They were numbered from the left of figure 1 to the right. The bottom of the beam was made with chloride-free concrete while the upper part had 0.7% of chlorides in the mixing water.

All the bars were de-rusted and degreased and the repaired zones were primed with System 1, 2, 3 or 4 described below to manufacturer specifications. Electrical wires were welded to one end of each segment for subsequent connection to external instruments, duly insulating the welds with epoxy resin and tape.

Casting itself consisted in a three-step process: first the bottom was casting with chloride-free concrete. The sides of the repaired area were casting with water containing 0.7% chloride ions (by cement weight) in the form of calcium chloride (CaCl₂. After 8 d curing humidity chamber, the centre and top (repaired area) of the specimens were filled with the repair material to simulate patching and cured for a further 28 d. The solids used to cast the beams were mixed with water containing 0.7% chloride ions (by cement weight) in the form of calcium chloride (CaCl₂). This proportion was slightly above the steel depassivation threshold which is usually assumed to be between 0.4-0.6%. The corrosive action was confirmed by measuring the corrosion rate from the beginning of mixing registering initial values above 10 μ A/cm².

In the first step of specimen casting described above (beam bottom and sides), the concrete used was made with ordinary portland cement (OPC), a water/cement (w/c) ratio of 0.65 and cement: sand: gravel proportions of 1:2.9:3.2. The 2330



Figure 3. Segmented reinforcing bar to study galvanic current.



Column with corrosion stains at different heights

Patch types tested

Figure 4. Columns on a building in Mexico repaired using different systems.

kg/m³ standard mortar used as a reference repair material in the beam centre was prepared with 530 kg/m³ of the same OPC as in step 1, a w/c ratio of 0.42, a cement: sand ratio of 1:3 and 1.5% (cement wt) of plasticiser. This central area is referred to hereafter as the 'repaired zone'.

The differences distinguishing the various tests consisted in varying: 1) the type of primer or bonding agent used between the new and existing material; 2) the chloride concentration in the mix; and 3) humidity and temperature.

The primers used were as follows:

- o System 1: no primer, standard alkaline repassivation with the reference repair mortar.
- o System 2: single component, high Zn content epoxy resin primer (with 74,8% likely zinc powder at the interface between the hardened primer and the reinforcement) with cathodic protection action. The dry thickness of the primer applied in two coats was estimated by stereomicroscopic means of 330 μm.
- o System 3: combination barrier/inhibition system consisting in acrylic dispersion with dicyclohexylamine to inhibit corrosion, OPC additioned with chromium oxide as an anti-oxidising pigment and sodium nitrate (NaNO₃) as a corrosion inhibitor.
- o System 4: barrier mechanism based on a twocomponent epoxy resin and hardener.
- Chloride concentration: chloride ion was added to the concretes at a concentration of 0.7%, the threshold value found to induce depassivation, or higher.

The specimens with segmented bars after the 28 days of curing were subsequently stored under the environmental conditions listed below, in order to study the galvanic behaviour under a range of moisture contents [16,19].

1. Repair (8 days after casting).

2. Curing (24 d).

- 3. Storage at 80% to 90% relative humidity (127 d).
- 4. Partial immersion (186 d).
- 5. Air drying (1292 d).
- 6. Storage at 85% RH (1382 d).
- 7. Storage at 100% RH (1492 d).
- 4. *Existing structures studied*: as the existing structures bore no segmented reinforcement, galvanic current could not be measured, although corrosion rate readings were taken with a guard-ringed corrosimeter¹ (see description in a subsequent sub-section). Two case studies were conducted for the present review:
 - a. A building in Mexico whose columns (figure 4) exhibited corrosion at different heights on different sides. As the figure shows, the primers tested were based, in one, on a corrosion inhibitor, in the second on barrier formation and in the third zinc powder as cathode protection. Bonding agents between the new and existing concrete were likewise used.
 - b. A viaduct on Spain's motorway AP-1 patch² as part of the EXTREPHOR project [25], on which in situ chloride content measuring methods were tested and corrosion rates determined before and after repair. An overview of its split-level junction is shown in the uppermost photograph in figure 5. The middle strip of the figure depicts three stages of pier shaft and the bottom strip three of pier cap repair. The areas affected included the tops of beams and pier caps and shafts. The area repaired extended 10 cm beyond the steel corrosion damage visible when the concrete cover was removed, even where the concrete exhibited no deterioration in those adjacent areas.

¹ GECOR10 corrosion rate meter.

² Repaired by RETINEO.



Figure 5. Viaduct on motorway AP-I (Spain) patch-repaired.³

The repair-protection procedure applied entailed the use of:

- a primer with a corrosion inhibitor, applied to the reinforcement before concrete regeneration with a repair mortar.
- a thixotropic repair mortar bearing organic corrosion inhibitors.
- a fluid mortar in certain areas where thixotropic mortars could not be used.
- a water vapour-permeable, elastic, anti-carbonation, water- and aggressive atmospheric agent (CO₂ – SO₂)-repellent acrylic resin paint.

2.2. Techniques

This sub-section discusses the techniques used in the EXTRE-PHOR [25] and XRF-CODE [26] projects⁴.

2.2.1. In situ measurement of concrete carbonation and chloride content

Carbonation can be readily detected with a pH indicator (although phenolphthalein has been identified as cancerogenic, alternative safe substances are now available) applied in situ with no need to retard the sequence of damaged concrete removal. Not all carbonated concrete has necessarily to be removed, however, because the corrosion rate may be low, not been needed the concrete removal. That is, in carbonated concrete the measurement of the corrosion rate is a critical information in order to preserve the original concrete.

Where chlorides are present, the corrosion rate denotes the risk involved, although the chloride concentration in regions

not initially targeted for repair should also be ascertained. Chloride content is much less readily detected in situ than carbonation, however. The sole suitable colour indicator, silver nitrate, routinely delivers erroneous results in situ, among others because it calls for a number of hours of exposure to ultraviolet rays to distinguish between the dark tone of the silver and the pale hue of silver chloride.

As one of the aims of the EXTREPHOR project was to find an in-situ method for analysing chloride content, a number of chemical approaches were studied:

- quick chloride analysis kits used to analyse water quality.
- the chloride ion selective electrode method.
- the swimming pool salinity measurement method.
- the turbidity method.

In light of the drawbacks to these methods for on-site use during repair operations, the literature was reviewed for possible non-destructive methods applicable to concrete. The most promising proved to be X-ray fluorescence (XRF), in use for some time in laboratories and for which handheld devices were beginning to be commercialised (figure 6). Its suitability was studied as part of the XRF-CODE project [26]. The methodology involved appeared to be simple, for the samples did not necessarily require pre-treatment, given that the X-ray beam could be focused on the concrete surface directly. Such devices are fitted with screens that display and record the readings indicative of the proportions in the sample of certain pre-selected elements.

2.2.2. Electrochemical measurements

Essentially two types of measurements are used to study galvanic couples:

- galvanic current (I_{galv}).
- corrosion rate (I_{corr}).

³ By RETINEO.

⁴ Projects implemented by RETINEO and coordinated by Luis Ortega Basagoiti in conjunction with the Eduardo Torroja Institute's Reinforcement Corrosion research team, headed at the time by the first author of this paper.



Figure 6. Handheld XRF device measuring chlorides in a concrete specimen previously exposed to natural seawater.

Although the two measurements are sometimes mistaken for one another or deemed to be synonymous they actually deliver different types of results, as noted in the discussion below. One of the primary differences is that $\rm I_{galv}$ is divided by the area of the anode whereas $\rm I_{corr}$ is divided by the total (anode+cathode) area. They cannot therefore be compared without normalising one of the two currents to the area used in the other.

Measurement procedures included the following.

Galvanic current (I_{galv}) was measured with a zero-resistance ammeter (ZRA) used to take separate anodic and cathodic readings in each segment. The ZRA maintains a null resistance between the two electrodes and measures the current between them at the mixed potential. Measurement timing varied with the type of test.

- In diffusion cell samples the electrodes could be uninterruptedly connected or otherwise and corrosion rate measured up (Icorr, up) or down (Icorr, down) -stream of either the unconnected or the connected (Icorr and Igalv) electrodes.
- o In the laboratory-prepared beams with all the segments connected, the ZRA was inserted between segments 1

and 2, conventionally deeming the wire connected to segment 1 the cathode (negative pole) and the one connected to segment 2 the anode (positive pole). In other words, when Igalv was positive under the conventional layout, segment 2 was anodic relative to segment 1 and vice-versa: when the Ig reading was negative, segment 2 was cathodic relative to segment 1.

After that first reading was recorded, the wires between segments 1 and 2 were reconnected and the ZRA was inserted between segments 2 and 3, with segment 2 as cathode and segment 3 as anode. This same procedure was repeated to measure the Igalv in the six inter-segmental intervals, interpreting the signs on the values as described. Each segment's contribution to the total Igalv was found by assigning the first reading to segment 1 and the algebraic difference between that and the following value to segment 2 and so on. Since each beam bore both one continuous and one segmented bar, electrochemical analyses could be conducted for each area of the beam separately and its anodic or cathodic behaviour determined.

a) Further to routine practice, corrosion rate (I_{corr}) was measured in terms of polarisation resistance (R_p), also known as linear polarisation resistance (LPR), which at the same time delivers corrosion potential (E_{corr}) and environmental resistance (R_e) data [27]. The technique deployed consisted in applying a low intensity current to the bar and measuring the change in potential induced. R_p was found as the $\Delta E/\Delta I$ ratio and corrosion rate, I_{corr} with the expression:

$$I_{corr}\left(\frac{\mu A}{cm^2}\right) = \frac{26}{R_p Area} \tag{1}$$

Given that in large specimens such as beams or columns or large on-site members the area polarised is unknown, R_p must be measured with a specific corrosion rate meter. Here the instrument used throughout, a handheld device⁵, was fitted with a guard ring that confined the current to a specific area [28]. More specifically, the measuring probe for the central auxiliary electrode housed a guard ring governed by two tiny electrodes inserted between the central and guard electrodes to control the current in the latter, as shown in figure 7. The technique consisted in applying a low intensity current to the reinforcement as depicted in the figure.



On-site corrosion rate meter Probe with external guard ring Figure 7. Handheld⁵ as used on site and probe with guard ring, central auxiliary electrode and control electrodes between these two.

The corrosion level criteria applied were as set out in RILEM recommendations [29] and given in table 1.

 TABLE 1.

 Corrosion levels and reinforcement condition by corrosion rate value.

| Corrosion level | µA/cm ² | µm/year | Rebar condition |
|-----------------|--------------------|---------|--|
| Negligible | < 0.1 | < 1 | Passive |
| Low | 0.1 – 0.5 | 1 – 5 | Depassivated, low humidity concrete |
| Moderate | 0.5 – 1 | 5 – 10 | Active corrosion, medium humidity |
| High | > 1 | >10 | Large areas corroding in wet concrete |

3. results

Results are given here only for the tests relevant to the primary aims of the study, i.e., to identify the areas in need of repair and subsequently monitor repair efficacy.

3.1. Diffusion cells

The findings set out in figure 8, drawn from earlier reports [22,24], illustrate the mechanism governing galvanic couple formation. The cell (figure 2) contained a 0.1 M NaOH solution to induce cathodic behaviour in the metal. A bar made of the same steel was placed in a 0.05 M FeCl₂ solution (to intensify anodic behaviour) in the other chamber, deaerated with continuously flowing nitrogen.

The figure shows the corrosion potentials before and after connecting the electrodes. The test was also designed to study the effect of inserting electrical resistance into the circuit to simulate different degrees of concrete saturation. Before connecting the steel, the resistance obviously had no effect, with the anode exhibiting values of around -600 mV (calomel) and the cathode of around -400 mV, irrespective of the resistance in the external circuit. After connection, the rebar was not polarised until resistance dipped below 10⁴ ohms. At lower values, anodic and cathodic potential tended to converge, as expected, although they did not reach the same value even at very low resistance, for the resistance in the concrete disk was too high to accommodate such concurrence.

3.2. Segmented reinforcement

Results for patch repair of segmented rebar were also extracted from earlier reports, in this case on concrete beams and slabs. Figure 9 shows the variation in galvanic current density (divided by anode area) with the cathode area/anode area (Sc/Sa) ratio [20,21,24]. The figure reproduces separate results for three tests conducted on members with widely differing geometries, with bars set linearly or in parallel. When the ratio rose, i.e., when the anode value declined or the cathode value rose, the galvanic current rose with it. In linear arrangements the initially exponential rise flattened at higher Sc/Sa ratios (i.e., tended to an upper limit) and where the electrodes were set in parallel, the rise was linear. The most significant finding was that the currents did not exceed an anode value of around 30 μ A/cm² and when the anode was greater than or equal to the cathode the currents were comparatively small, at around 1 µA/cm². Of the several inferences that could be drawn from those data, the one of greatest relevance here is that (in the absence of data from other authors) inasmuch as the values concurred for three separate tests, they may very likely be liable to extrapolation to other setups. The expressions given in the figure may, then, be used for the purposes of prediction.

Two trends are depicted in figure 10: the rise in galvanic current with the Sc/Sa ratio in one of the cases analysed previously [24] and the ratio between the pre- and post-connec-



Figure 8. Effect of resistance in the circuit on anode and cathode potential before and after connection (Sc/Sa is the ratio between the surface of the cathode to the surface of the anode).



Figure 9. Galvanic current (I_{galv}) vs cathode/anode area (Sc/Sa) ratio [20,21,24].



Figure 10. Variation in pre-/post-connection anode current (Icorr,a) ratio and in galvanic current (Igalv) with cathode area/anode area (Sc/Sa) ratio.

tion Icorr,a (divided by the anodic area only) [24], (cathodic efficacy, χ):

$$\chi = \frac{I_{corr,a} \ after \ connection}{I_{corr,a} \ before \ connection}$$
(2)

As that ratio reveals the extent of corrosion intensification when larger cathodes are connected, it can be used to assess the effect of Sc/Sa in terms of its effective value, i.e., the value of the rise in corrosion in the anodic area. Galvanic current accounts for only part of the total, as indicated by the expression:

$$I_{corr} = I_{micro} + I_{galv} \tag{3}$$

The findings showed that corrosion was not accentuated in the anodic area when larger cathodes were connected. The findings might even be deemed odd, denoting high efficacy in area ratios of 1 and insignificant efficacy where such ratios were greater or less than 1. The explanation lies in the position of the segments connected (the test was conducted on a slab with parallel bars). In other words, circuit resistance had an additional impact whereby efficacy was governed by the combined action of the area ratios and circuit resistance rather than by cathode size alone.

Other tests were conducted on prismatic specimens such as shown in figure 3 [16,19], where the central area of the segmented bar was repaired. In those trials the variations in all the electrochemical parameters with time, environmental temperature and humidity were monitored and the three types of reinforcement primers described above and plotted on the figures 11 to 14, were studied.

Total galvanic current values (not divided by any area) for the seven segments embedded near the top of the member (the three centre-most of which lay in the repaired zone) are given in figures 11, 12 and 13. Measurements were read 3 days after repair (24 d after manufacture), 103 days after repair and storage at 80% to 90% RH and 1492 days after repair, >200 days of which at over 95% RH. The environmental conditions prevailing during the test were sequenced as listed in the sub-section on materials.



Distance of the steel segment from the end of the bar (cm)

Figure 11. Total galvanic current (Igalv) in the seven segments of the bar positioned in the patch repair zone 3 d after repair (anodic behaviour in the repaired zone observed only for the cathodic protection system consisting in zinc powder in polymeric matrix) [19].



Figure 12. Total galvanic current (Igalv) in the seven segments of the bar with the patch repair zone 1492 days after repair (all systems observed to have very low current) [19].



Distance of the steel segment from the end of the bar (cm)

Figure 13. Total galvanic current (Igalv) in the seven segments of the bar with the patch repair zone 3 days after repair [all systems observed to have very low current with incipient anodic values in the outer-most segments, possibly attributable to carbonation) [19].

The inference drawn from these findings is that when an area is repaired, the segments in the adjacent areas (in the presence of 0.7% chlorides, somewhat higher than the corrosion induction threshold) begin to corrode, albeit very slightly and for a short period of time. After a few days the currents change sign, adopting negligible values irrespective of subse-

quent temperature and humidity conditions. A comparison of the findings for the primers showed that whereas the ones that formed barriers only or bore both barrier agent and inhibitor exhibited very low galvanic currents, the one containing zinc powder logically afforded cathodic protection, inducing the adjacent areas to act as cathodes.



Figure 14. Variation in galvanic current over time (test conditions with time were listed in the Experimental chapter) in the repaired zone, at the repair/existing concrete interface and in the unrepaired zone (left: total galvanic current, significant only in the first few days; right: corrosion rate $(< 0.1 \mu A/cm2 after the first two test conditions)$ [19].



Figure 15. Variation in galvanic current with corrosion rate in the reference specimen [19].

Figure 14, which depicts the reference prismatic specimen [19], confirms the nearly nil galvanic currents and corrosion rates in the repaired central zone, the segment at the interface with the existing concrete and the one in the existing concrete additioned with 0.7% chlorides. Despite the successive changes in humidity and temperature applied, the findings showed nearly nil corrosion except in the first measurement after repair.

Figure 15, in turn, graphs the relationship between galvanic current and corrosion rate in the reference specimen segments after the last, 109 days test period (around 4.5 years after casting), during which the specimen was stored at 40 °C and >95% RH. Except in one segment, the galvanic current amounted to 20% or less of the corrosion rate. All these findings denoted negligible risk of corrosion intensification, whether or not the steel was primed, although the zinc powder primer was indisputably effective for it afforded the adjacent areas extra protection.

The use of bonding agents [15, 18] between the new and existing concretes was found to be beneficial, for they also reduced corrosion rates in the adjacent areas slightly.

3.3. Repaired viaduct

Figure 16 gives some of the high corrosion values measured in the pier cap on the viaduct prior to repair and the readings

around the zone on a pier under repair denoting passivity in the adjacent regions.

4. DISCUSSION

The discussion below of some of the basic principles of galvanic current relevant to patch repair is followed by remarks on primer action and the extent of concrete removal and repair recommended. It also describes detection techniques, the key to ensuring long-lasting repair.

4.1. The galvanic couple: basic characteristics

A galvanic couple is defined to exist when two metals come into contact in the same electrolyte or when a potential difference arises in one and the same metal due, for instance, to surface roughness. A current is then generated between the two metals or between the areas with different potential in the same metal to offset the difference in potential. One metal or area (the anode) donates electrons to the other (cathode). The resulting current (I) follows Ohm's law:



Figure 16. Left: corrosion values on the viaduct pier cap prior to repair; right: corrosion values during repair on a viaduct pier.



Galvanic couple on parallel bars

Galvanic couple on the same bar

Figure 17. Left: galvanic currents in parallel bars; right: galvanic current in linear bars.

I=dE/R, where dE is the difference in potential and R circuit resistance.

As figure 17 shows, resistance in the medium varies depending on whether the metals or zones are linear or parallel, as does galvanic current distribution, which is uniform where the electrodes are parallel and tends downward with rising distance in linear layouts. The parallel couples depicted simulate situations where rebars parallel to the repaired bar are electrically connected to it across stirrups, whilst linear couples are generated on the repaired bar in areas adjacent to the repaired zone. The latter may also be found on the sides of the specimen or member where parallel couples may exist as well.

Another essential principle is that steel corrosion in concrete develops primarily in response to microcells [12,20], i.e., as discussed in the results section, the corrosion rate is governed primarily by the many cells generated in the corroded area, whilst the galvanic current in a macrocell accounts for only a small proportion of the total current (figure 18 and Equation [3]).

To put it another way, given the high electrical resistance in concrete, corrosion ensuing from the creation of electrical circuits through the material is the result of circuits covering short distances (microns to cm) rather than of circuits involving ion movements across longer distances. The exception is underwater concrete, where the external medium favours the circulation of galvanic currents.



Icorr = Sa+Sc= corrosion rate (Icorr,total)

Figure 18. Corrosion generated primarily by microcells (intensity generally lower in macrocells; cathodic area limited by electrical resistance in circuit).

That explains why the action of patch repair-induced macrocell couples is confined to a small distance and scantly significant along the interfaces of repaired/existing zones, where they persist only in the short term. If the areas adjacent to repaired zones corrode, it is either because they contained chlorides at higher than the critical concentration or were carbonated.

4.2. Scope of galvanic currents in patch-repaired zones

Figures 11 through 14 show that galvanic current is detected in the first few days after repair in the areas closest to the interface but not at all in more distant regions. Two inferences may be drawn from those data.

1. Prior to patch repair the severely corroded area may cathodically protect the closest adjacent areas. In other words, the corroded areas act as sacrificial anodes for the

adjacent areas. That was verified in the study of the column (figure 4), where anodic and cathodic zones were detected along one and the same bar and the effect observed to be more intense in the lower, more corroded region.

2. The cathodic protection afforded by corroded areas vanishes when they are repaired whilst the reverse effect, conversion to a cathode with intensified corrosion in the unrepaired area, is short-lived (figure 14). Consequently, such adjacent areas undergo post-repair corrosion not because a cathode was created in the repaired zone, but due to the presence of chlorides at higher than critical concentrations or the persistence of carbonation.

In other words, failure to remove all the contaminated concrete during repairs has implications not because the postpatched passive zones intensify corrosion, but because prior to repair part of the area failed to corrode as a result of the sacrificial anode role played by the corroded areas. When such 'sacrificial anodes' disappear, the contaminated areas previously protected by that galvanic action begin to actively corrode.

The tests prove that the scope of both the prior cathodic protection and of its subsequent reversal is restricted to a distance of a few cm. In submerged members, the area involved may be greater due to the lower electrical resistance of the medium. In addition, it depends on the existence or otherwise of an external liquid environment where the currents can circulate and of course on the conductivity of that liquid, which is very high in the case of seawater, where significant galvanic effects may arise.

4.3. Primer action

One way of completely eliminating any possible albeit limited cathodic action in the newly repaired zone is to apply a primer to the repaired rebar or bonding agents to interrupt the cross-concrete circuit. Primers are likewise recommended by manufacturers to raise the bonding strength of the new material, for the ribs on the existing reinforcing steel may have partially or wholly worn away. Primers improve bonding, then, constitute additional protection in the repaired zones and can eliminate potential macrocell couples. Such couples may also be eliminated with agents designed to enhance bonding between the existing concrete and the new repair material [18].

The primer action illustrated here in figures 11, 12 and 13 [15,16,19] was shown to depend on the nature of the primer. All these products eliminated or minimised the galvanic currents appearing in the early days after repair, while the epoxy-zinc primer even inverted the effect, for it afforded cathod-ic protection in the unrepaired zones. That cathodic action ceased when all the zinc in the primer oxidised but sufficed to retard any initial corrosion in the adjacent areas, even where contaminated. Upon depletion of the zinc, corrosion would begin in those areas, however.

The epoxy primer whose sole effect was to generate a barrier eliminated the galvanic current altogether, although no significant change in behaviour relative to the reference was observed, for where the adjacent areas were highly contaminated, they corroded to much the same extent as they would in the absence of the primer. Primers bearing an inhibitor might be thought to intensify the cathodic effect in the repaired zone. The findings for the product tested here, however, showed the effect to be insignificant relative to the reference, where the new material passivated the steel in a manner similar to that observed in the reference.

That attests to the importance of identifying not only the type of primer, but the application conditions in the repair, since small manufacture or behavior differences can mislead the understanding. This was the case of the repaired columns in a public building in México (figure 4) where were tested primers of the same type (cathodic or inhibitor or repassivant or barrier) but from different manufacturers, or different qualities from the same manufacturer. These differences, however, were not reflected into the galvanic currents recorded between repaired and non-repaired zones that were very similar in all cases and irrespective of the size of the repaired (cathodic) to non-repaired (anodic) zones.

The primers of the same type (inhibitory, repassivating or barrier) but of varying quality or sourced from different suppliers used in the example in figure 4, a column on a government building in Mexico, exhibited significant electro-chemical differences, further to table 2 in reference [15]. That circumstance might lead to misinterpretation of the effect of the respective primers on the galvanic behaviour presumably induced by repair.

4.4. Detection of contaminated areas⁶

As noted in the introduction, when damage (cracks and rust stains) is initially detected, with a view both to cost considerations and to ensuring minimal alteration of the integrity of the original concrete, the general trend is to repair only areas with visible damage. A balance must be struck, then, between the avoidance of the need for re-patching every so often in areas newly depassivated when passivity is restored in visibly damaged, but subsequently repaired zones, and structural alterations due to concrete removal. That issue is particularly problematic where the concrete is neither obviously cracked nor weakened. More than that, the structural behaviour of the repaired structure, a question not addressed here, may be significantly impacted by the properties of the existing and new material. Hence the importance of clearly delimiting the zones in need of de-rusting and restoration, even where they exhibit no outer damage.

That very basic purpose of inspection may be broached in two ways:

- a) by analysing chloride content or carbonation in the areas adjacent to the one to be repaired and removing concrete until non-contaminated material is found,
- b) by measuring corrosion rate electrochemically both before and after repair.

Given the direct relationship between cost and extent of repair, owner and hired contractor are bound to have different opin-

⁶ This issue of repairing sufficiently without overdoing was of such concern to Luis Ortega Basagioiti that it led him to propose two research projects on behalf of RETINEO, one (EXTREPHOR) (26) funded by the Ministry of the Economy and Competitive Affairs (INNPACTO Programme) and the other (XRF-CODE) [27] by the CDTI (Spanish Centre for Industrial Technological Development). The aim was to explore technologies that would most effectively and economically identify contaminated areas *in situ*.

ions about the economic dimension of patching. As in any other field where virtue lies in the middle ground, defining general rules or quantifying with no heed to the specific case at hand is no easy task, for social cost and heritage value may tip the scales toward more or less extensive repair. In a visibly damaged concrete with heritage value, for instance, the ideal approach would be to remove as little concrete as possible, even at the risk of subsequent depassivation in other areas. In concretes not deemed to be cultural assets, in contrast, all the material where contamination is suspected should be removed to prevent the reinforcement from deteriorating further, providing structural behaviour is not compromised. That calls for detailed inspection based on more than mere visual observation.

4.5. On-site analysis of carbonation and chloride content

The interest to find out how much concrete is necessary to removed led to study different site methids to analyse chlorides. Those studied are summarized in table 2 below.

TABLE 2.

Types of on-site chloride analysis tested.

| | ADVANTAGES | DRAWBACKS |
|---|--|---|
| Quick chloride analysis kits used to analyse water quality | Accurate if the right range is found | A powder sample is required. The powder must be dissolved in acid or water. It calls for laboratory procedures (Mohr or diphenylcarbazone method). The kits are for prede fined chloride ranges. |
| Chloride ion selecti- ve electrode method | Accurate if electro- de pre-calibrated | A powder sample is required. The powder must be dissolved in acid or water. The electrode is expensive. |
| Swimming pool sali- nity measurement method | Less expensive than the selective electrode method | The sample must be prepared in the same manner. It measures not chlor de but sodium. |
| Turbidity method | The simplest of the chemical proce- dures | It is qualitative only. The sample must be prepared in the same manner. |
| Silver nitrate co- lorimetric method directly on concrete | Colour-based and therefore very simple | - The colours are not clearly distinguishabl in on-site scenarios. |
| On-site FRX | Immediate, on-site results The operator needs no knowledge of chemical analysis. | The instrument is expensive.The instrument must be calibrated. |

The conclusions drawn from a study of the various techniques for detecting chloride contamination in the remaining concrete

included the following.

- 1. One basic issue is whether to work directly on the concrete as it stands or take a sample that needs to be subsequently ground and dissolved:
 - a. in acid to determine total chlorides
 - b. in water to determine unbound chlorides. The most suitable procedure for such analyses is set out in RILEM's recommendation 'Analysis of water-soluble chloride content in concrete' [30], which entails dissolving the sample in 50 mL of distilled water and filtering immediately after just 3 min. At longer times part of the total chlorides may dissolve.
- 2. The kits designed for field measurements call for knowhow generally lacking among structural repair personnel, namely a certain minimal understanding of chemistry and toxic substance handling. The Mohr method or use of diphenylcarbazone involved in their deployment calls for specialised personnel. And as these kits are intended for specific detection ranges for any given silver nitrate concentration, multiple analyses may be needed to find the right range.
- 3. The turbidity method (acid medium additioned with silver nitrate) is somewhat simpler than the kits, for as it is qualitative only test tubes can be prepared in advance and the ground cement simply added in situ. The personnel involved must nonetheless be qualified to interpret the turbidity observed or be furnished with standard samples (figure 19) for, as inferred by the figure, drawing distinctions is not always straightforward.



Figure 19. Turbidity test based on nitric acid and silver nitrate.

4. The selective chloride ion electrode method is certainly promising for it calls for no chemicals except acid if the aim is to determine total chlorides. Samples can be placed into pre-prepared test tubes, although they must be weighed, for as the trial is quantitative the results are referred to sample weight. That, in turn, entails bringing a small balance to the worksite.



Figure 20. Selective chloride electrode test.



Laboratory specimens

On-site concrete

Figure 21. Colour-based silver nitrate indicator chloride test on concrete.

- 5. The electrode-based salinity measurement system used to monitor swimming pools (figure 20) does not measure chlorides per se, but sodium or conductivity. While it is much less expensive, then, the device is not recommended for it only measures chloride directly if it forms part of sodium chloride. It also calls for prior sample weighing and dissolution in acid or water.
- 6. The method involving spraying silver nitrate directly on the concrete is not recommended either, due to its scant sensitivity in on-site concrete. Figure 21 depicts in the left the case of specimens submitted to chloride diffusion in the laboratory (the white zones are those where the chlorides arrive during the test time) and in the right is shown an area of the pier cap on the viaduct described earlier where the silver nitrate utterly failed to distinguish between the chloride-contaminated and non-contaminated areas. The front is typically difficult to distinguish on site, where contamination is irregular.

All these limitations informed a search for alternative methods. In light of the incipient development at the time of handheld X-ray fluorescence (XRF) instruments, a second CDTI project was applied for (XRF-CODE) [26] to study the feasibility of their use for this purpose. The instrument initially used is depicted in figure 6.

The widespread use of XRF for elemental analysis had been extended by the authors' team to analyse chloride profiles in concretes. As up to 20 samples ground mm to mm in depth are required, drawing such profiles entails multiple testing. The acquisition of an X-ray diffractor and fluorescence facility⁷ made it possible to analyse 48 samples simultaneously [31], greatly enhancing test efficacy. The drawback to the procedure is that as the composition measured is a percentage

7 Fluorescence facility of the IETcc.

of all the compounds in the sample, it calls for pre-calibration against standard samples with known chloride contents. Figure 22 calibrates portable XRF-detected chloride concentration (in ppm) against the potentiometric findings for three standard samples with widely differing values and for the two chloride profiles plotted in figure 23. According to the latter the handheld XRF delivered readings somewhat lower than the potentiometric method. After optimisation during the project, the measuring procedure yielded a very acceptable correlation. Handheld XRF devices facilitate on-site repair, for the readings can be interpreted by personnel with no specialised chemical analysis training.

4.6. Corrosion rate measurement

Both as a supplement to carbonation and chloride analyses and in its own right, corrosion rate measurement provides indispensable information during inspection as well as during and after repair to confirm efficacy, defined in terms of the 0.1 μ A/ cm² ceiling rate set out in the respective RILEM recommendation [29]. This technique can be used for continuous and comprehensive monitoring throughout, i.e., during and after repair. This applies even if the repair material or the coating is polymer-based, because if these materials are insulators for the electrical current, this is detected by the impossibility to measure the corrosion rate, but precisely if the corrosion rate can be measured it is a sign of deterioration of these materials. That is, the corrosion rate measurement is a manner to detect integrity of epoxy/polymer-based repair materials: as soon as their resistivity lowers and measures are feasible, it is an indication on its deterioration.

Corrosion rate testing for comparison of the findings to the aforementioned limit must be conducted in moist concrete, inasmuch as the values may dip to below 0.1 $\mu A/cm^2$ in dry material, for corrosion requires moisture. The concrete





Figure 22. X-ray fluorescence/ traditional potentiometric titration procedure calibration in standard samples bearing known chloride concentrations and for two chloride profiles.



Figure 23. One of the chloride profiles used in the preceding figure, showing the difference between XRF and potentiometric values.

is sufficiently moist if exposed to rain or seawater spray. If the concrete does not come into direct contact with water or is exposed to high temperatures possibly favouring evaporation of its water content, it may not retain sufficient moisture to support corrosion. Consequently, testing should be conducted in the winter or after abundant rainfall.

In addition to the impact of climate on concrete moisture [32], the project findings revealed that certain repair materials exhibited corrosion rate values >0.1 μ A/cm². Although the possible reasons were not explored, they must have had to do with the inhibitors added or differences in pH relative to OPC. In such cases testing must be repeated some weeks later to verify whether the values drop below the upper Icorr limit defined.

The measuring procedure is summarised briefly below.

Pre-repair - corrosion rate measurements detect the most severely corroded areas, i.e., the location of anodes (where corrosion rate is highest) and cathodes (lower rates), as depicted in figure 16, and verify whether the cathodic areas are passive ($I_{corr} < 0.1 \mu A/cm2$) or have a lower Icorr but are corroding. Merely comparing the values observed suffices to identify the areas most severely affected irrespective of their appearance



Figure 24. Up: corrosion rate values for a viaduct; and down: temperature values for the same timeframe (note the increase in I_{corr} with temperature and the similar pattern of variation of the two parameters).

and on those grounds establish the most suitable order for repair.

During repair - once the areas where the concrete must be removed are defined, measurements may be made in the adjacent regions (figure 16) to verify possible changes in behaviour after the contaminated concrete is removed and the reinforcement cleaned. A rise in the corrosion rate in the adjacent areas would be indicative of incipient depassivation and help determine the advisability or otherwise of using a primer or bonding agent to eliminate or mitigate the galvanic effect of the repair.

Post-repair - the test should be run to verify that none of the areas involved has an I_{corr} value that would denote more or less immediate future deterioration. In the viaduct used as an example here, such verification testing revealed that the corrosion rate did not exceed 0.1 μ A/cm² anywhere in the structure, enabling owners to substantiate repair efficacy.

Corrosion rate sensors indisputably constitute the most effective way to monitor structures in the long term, a subject explored in the strategic philosophy chapter of the aforementioned projects [25,26]. The advantages/disadvantages of sensors were analysed in response to the difficulties they posed to owners to interpret the readings and handle the data, for corrosion rate changes with the weather and interpretation

requires a fair degree of specialisation. The data for a viaduct plotted in figure 24 show that corrosion rate is impacted by (i.e., rises with) temperature. Events such as electric storms, in turn, may induce variations in magnetic conditions, favouring the appearance of outlier values that must be discarded or even causing data measurement or transmission facility outages. Where sensors are used, their interpretation should be guaranteed by the supplier as a service, or the owners should be ensured access to the respective artificial intelligence algorithms.

5. CONCLUSIONS

The most prominent conclusions to be drawn from the foregoing are set out briefly below.

 Patch repairs may fail to remove all the contaminated concrete, risking further reinforcement corrosion that would require successive interventions. That circumstance lies at the root of the dilemma of how much to repair. In the absence of severe structural implications, that owner decision should be informed by expert opinion and subject to monitoring the repaired structure.

- 2. None of the tests conducted by the authors to study the behaviour of galvanic couples, specifically those generated by patch repair, has yielded evidence that such action intensifies corrosion in the adjacent areas. What was noticed is that the adjacent zones start to corrode because they are contaminated with chlorides and that the repassivation of the repaired zone does not enhance the corrosion of the adjacent zones, except in the first days after repairing. Simply the repair halts to act as sacrificial anode.
- 3. After repassivation, however, the damaged regions are observed to no longer act as sacrificial anodes for those in the immediate vicinity. The presence of contamination in the adjacent zones would consequently induce reinforcement corrosion.
- 4. Reinforcement primers and bonding agents of the types described here mitigate corrosion in the adjacent areas in the short term, although at longer times their effect is negligible.
- 5. Good pre-repair diagnosis to detect contaminated areas has been found to be a key to assessing the scope of repair, an issue with substantial financial and safety implications. The techniques to identify any residual contamination include:
 - a. carbonation testing, which is readily accessible given the availability of effective colour-based pH indicators.
 - b. chloride testing, which in contrast calls for laboratory analysis, although handheld X-ray fluorescence instruments highly compatible with fieldwork hold particular promise in this regard, despite the need for pre-calibration.
 - c. in-situ corrosion rate measurement, which is an essential technique that supplements the other two, for it determines whether the repair was effective by showing, immediately or several weeks after repair, whether corrosion rates lie below the 0.1 μ A/cm² recommended ceiling when measured in moist concrete.

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