Appliance of realkalisation in the conservation of monuments made of reinforced cement mortar and concrete

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Abstract

Conservation of monumental sculptures executed in reinforced cement mortar or in concrete has been a tough issue and, as such, remains unresolved. Corrosion processes, and primarily carbonation, result in pore solution's pH reduction. Such pH reduction leads to diminution or loss of an artificial stone's protective features in relation to its reinforcement, initializing electrochemical corrosion of steel. As opposed to traditional yet invasive methods of conservation, realkalisation makes re-enacting of high pH level possible – by reinstating an oxide film on the reinforcement that allows concrete to maintain its monohedral properties, and, above all else, to remain intact as far as original surface of an antique is concerned. The following article discusses electrochemical and diffusive realkalisation, their functioning, advantages and drawbacks. Examples of properly executed procedures have been given, as well as alkaline solution's' composition. During the research conducted over interventions in diffusive realkalisation, the author has considered and assessed pH level increase. Particular attention has been paid to assessing the pH increase, evenness of treatment, and its influence on the colour shift of impregnated material.

Abstrakt

Zastosowanie realkalizacji w konserwacji zabytków wykonanych ze zbrojonej zaprawy cementowej i betonu

Konserwacja zabytkowych rzeźb wykonanych ze zbrojonej zaprawy cementowej lub betonu stanowi trudny i wciąż nierozwiązany problem. Procesy korozyjne, a przede wszystkim karbonatyzacja wpływają na obniżenie pH cieczy porowej. Spadek pH skutkuje zmniejszeniem lub utratą właściwości ochronnych sztucznego kamienia w stosunku do zbrojenia, inicjując proces elektrochemicznej korozji żelaza. W przeciwieństwie do tradycyjnych inwazyjnych metod konserwacji, realkalizacja umożliwia przywrócenie wysokiego pH, wpływa na odtworzenie warstewki tlenkowej na zbrojeniu, zapewniając jednorodne właściwości betonu, a przede wszystkim zachowanie nienaruszonej oryginalnej powierzchni zabytku. W artykule omówiono zasady działania realkalizacji elektrochemicznej oraz dyfuzyjnej, ich wady oraz zalety. Podano przykłady poprawnie wykonanych realizacji oraz składy roztworów realkalizujących. W przeprowadzonych badaniach nad zabiegiem realkalizacji dyfuzyjnej uwagę zwrócono na ocenę wzrostu pH, równomierność zabiegu, ponadto jego wpływ na zmianę koloru impregnowanego materiału.

To conserve monuments made of an artificial stone with concrete binding agent is to conserve spatially expanded composite comprised of sensitive concrete matrix, mineral aggregate deposits[1], as well as to make an attempt to stabilize steel reinforcement which is placed within. High pH of pore solution acts in a passivating manner on the surface of steel. However, with time, under the influence of corrosion[2], and, above all, of carbonation, pH decreases. Carbon dioxide, present in the air, is responsible for this process. It dissolves in pore solution and its subsequent penetration supervenes by capillary system. Carbon dioxide acts even when the concentration is low, although with its upswing, carbonation accelerates. Carbon dioxide reacts with callous cement leaven components merely in presence of moisture. The most sensitive of the components is calcium hydroxide which occurs in pore solution. It undergoes a chemical reaction with carbonic acid, giving calcium

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[1]   Depending on a size of an aggregate used, an artificial stone is defined as concrete or mortar. In the composition of a historical artificial stone, often imitating a natural one, apart from traditional quartz aggregate, we might encounter grits deliberately added by sculptors (marble, granitic or basalt) as well as mineral pigments.

[2]   Among main types of corrosion there are: leaching, carbonate, acidic, sulfate, magnesium, ammonium, intrinsic, frost and biological types. Aleksandra Gralińska-Grubecka, „Procesy korozyjne i konserwacja profilaktyczna rzeźb ze zbrojonego betonu”, in *Problemy muzeów związane z zachowaniem i konserwacją zbiorów,* ed. Lidia Staniek (Szreniawa: Muzeum Narodowe Rolnictwa i Przemysłu Rolno-Spożywczego, 2014), 40–48.

carbonate. Its cristallization results in sealing outer pores because calcium carbonate which forms there has 11 percent larger volume than the volume of Portland cement crystals is. Improvements in robustness and resilience to leaching are the beneficial sides of this reaction[3]. The disadvantageous side however is the fact that the pH of concrete lowers from 13,5 to as little as 9. pH dropping to a level of about 11,8 with free air access, and to about 11 with limited air access, results in decrease or deprivation of concrete's protective properties in relation to its steel reinforcement[4].

Sealing of external pores impedes access of subsequent carbon dioxide portions and moisture deeper into porous structure. Deeper down from the surface, carbonation reaches its front and, from there on, it starts to run at a very slow pace. In presence of a large aggregate and cracks, carbonation takes its course in an uneven manner. It is faster with a relative humidity of 50–75 percent though[5]. Carbonation hardly occurs in air-dried or in fully water saturated concrete. After the whole hydroxide has undergone its carbonation, pH is lowered to a level of 8,3. When hydroxide has depleted, hydrate aluminates and calcium silicates might undergo carbonation (C-S-H phases)[6].

A standard initial procedure in heritage monument estimation is to determine a front of carbonation (pH level) in its various parts. If it runs in front of reinforcement, a sculpture's condition can be considered stable, it's worse if it has reached a reinforcement's area though. With the latter, due to sectional damage of passive films, anode and cathode sectors come into being. There emerges iron oxidation in an anode sector, and reduction[7] in a cathode sector:

$$Fe \rightarrow Fe^{2+} + 2e^-,$$
$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-.$$
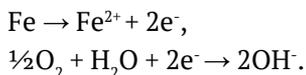
Pore solution, which is an electrolyte, conducts electricity. Weight flow of hydroxyl ions from a cathode to an anode is conveyed with a help of pore's

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[3] Hydroxide's solubility is 1,23 g/l whereas for calcium carbonate it is 0,015 g/l thus it is neraly 100 times lower than for the initial product.

[4] Lech Czarnecki and Peter H. Emmons, *Naprawa i ochrona konstrukcji betonowych* (Kraków: Polski Cement, 2001), 43.

[5] Adam M. Neville, *Właściwości betonu* (Kraków: Polski Cement, 2000), 519.

[6] Neville, *Właściwości betonu*, 518–519.

[7] Wiesław Kurdowski, *Chemia materiałów budowlanych* (Kraków: Uczelniane Wydawnictwa Naukowo-Dydaktyczne, 2003), 151.

solution, while electric charge flows in the form of electrons – from an anode to a cathode, through steel. As a result of electrochemical steel corrosion, a process of rusting begins. Its coating, having larger volume than steel, contributes to forming of significant internal strains whose relaxation manifests itself in micro scratches, cracks and, eventually, bursting of contiguous material (fig. 1–2). Corrosive transmutations usually begin from a surface of an object, slowly moving deeper and lengthwise, alongside scratches and cracks, constituting an inherent part of cement matrix.
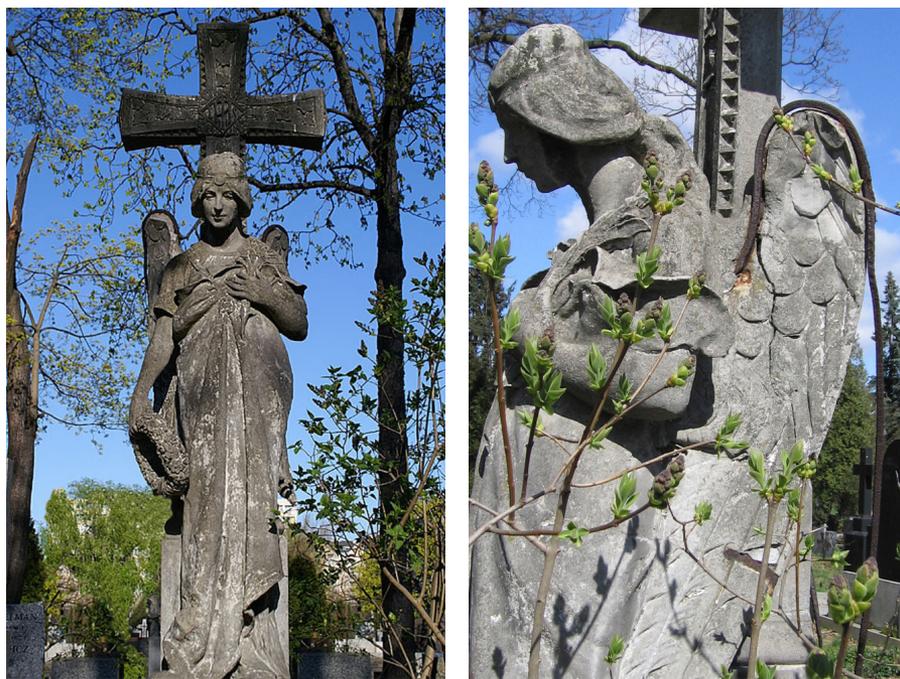

Fig. 1 and 2. Example of reinforcement corrosion caused by carbonation – the angel statue, dating 1895, from Augsburg-evangelical cemetery in Warsaw. Photo by M. Szulińska

Traditional methods of reparation – inadmissible from a restorer's point of view – involve removing degraded surface layer of an artificial stone until a healthy part of material is reached, cleansing corroded reinforcement, applying an impenetrable layer of an anti-corrosion specimen[8] and, subse-

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[8] The results of the research over anti-corrosion protection specimen have been concluded in the following publication: Aleksandra Gralińska-Grubecka and Jadwiga W. Łukaszewicz,

quently, new mortar or concrete, usually of different qualities in relation to the initial material. In need to avoid corrosion relapse, there are often used polymer-cement composites and, additionally, a micro-reinforcement with lower porosity, lower impregnability and higher mechanical endurance. Such action results in destroying monument's most valuable surface; furthermore, there are used materials of different properties than the original one[9]. Additionally, in areas placed in the vicinity of the repaired fragments, frequently new corrosive cells begin to develop, due to the fact that the areas supplemented with fresh mortar take over a role of active cathodes[10].

The above mentioned disadvantages can be eliminated by realkalisation which provides homogeneal properties of cement matrix and maintains valuable, original surface of a monument[11]. Another chance for non-invasive conservation is given by migrating corrosion inhibitors. Both methods are not bound to replace the necessity of removing some parts of degraded material, they are, however, able to reduce this unwanted interference to absolute minimum. Restorer's optimal choice is to synergically use realkalisation, migrating corrosion inhibitors, and sealing monument's surface with protective films[12].

Realkalisation

Durability prolongation for sculptures made of reinforced concrete is possible thanks to constraint of reinforcement's corrosion progress. This result can be acquired by using a procedure of electrochemical realkalisation. The

"A Comparative Study of Anti-Corrosion Products for the Protection of Reinforcement in Monuments", in *Concrete Solutions 4*th *International Conference on Concrete Repair*, eds. Michael Grantham, Viktor Mechtcherine, and Ulrich Schneck (Dresden: Technische Universität, 2011), 237–243.

[9] Materials used to fill cavities in monuments should fulfill a number of criteria, the most important being: close or even higher impregnability, close or even lower mechanical endurance, good adhesiveness, similar texture and colour. Jadwiga W. Łukaszewicz, *Badania i zastosowanie związków krzemoorganicznych w konserwacji zabytków kamiennych* (Toruń: Wydawnictwo UMK, 2002), 138.

[10] Czarnecki and Emmons, *Naprawa*, 7.

[11] Adam Zybura, *Zabezpieczanie konstrukcji żelbetowych metodami elektrochemicznymi* (Gliwice: Wydawnictwo Politechniki Śląskiej, 2003), 76–79.

[12] Gralińska-Grubecka, „Procesy korozyjne", 40–48; George Batis, Niki Kouloumbi, and Panagiota Pantazopoulou, "Protection of Reinforced Concrete by Coatings and Corrosion Inhibitors", *Pigment & Resin Technology* 29, no. 3 (2000): 159, accessed on 18th June 2011, doi:10.1108/03699420010334312.

procedure involves polarization of reinforcement with external direct current as well as processing concrete cover with electric field. Realkalisation results with profitable changes in pore solution's composition and reintroducing high pH which restores oxide film on the reinforcement[13]. Re-creation of oxide film results in discontinuing electrode reactions on steel[14]. The method was initiated in the 70s. in the USA, probed in part, and, thereupon, patented in 1987 in Norway, under the name NORCURE[15]. Practicably, the procedure involves covering outer surface of an object with cellulose fiber saturated in electrolyte solution, e.g. sodium carbonate or calcium hydroxide. There is a titanium mesh placed in the pulp. Wired up to the red pole, it performs the function of an anode, whilst the reinforcement constitutes a cathode, and hence it is connected to the blue pole. During realkalisation an external electrolyte penetrates concrete's pores and there proceeds diffusion of alkali inserted in pore solution, electrolysis on an auxiliary anode mesh as well as on surface of the reinforcement, ionic electromigration influenced by electromagnetic field and electro-osmotic injection of external electrolyte[16]. Hydroxyl ions which build on the surface of reinforcing bars, cause a gradual increase of alkaline concrete's reaction around the reinforcement[17]:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2\uparrow.$$
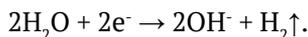
Concurrently, a disadvantageous side of this reaction is hydrogen emission. It poses a threat for the reinforcement, may very well cause hydrogenic embrittlement of steel and deteriorate adhesion between bars and concrete. Electric potential difference between negatively charged reinforcement and a positively charged electrode causes electromigration: cations H^+, Na^+, K^+,

[13] Zybura, *Zabezpieczanie*, 80.

[14] Mariusz Jaśniok and Adam Zybura, „Badanie składu cieczy porowej betonu poddanego elektrochemicznej realkalizacji", in *Kontra 2002 Trwałość budowli i ochrona przed korozją,* ed. unknown (Zakopane: Komitet Trwałości Budowli Zarządu Głównego Polskiego Związku Inżynierów i Techników Budownictwa, 2002), 97; Adam Zybura, „Szczególne metody zabezpieczeń obiektów", in *Nowe rozwiązania konstrukcyjno-materiałowo-technologiczne. Konstrukcje żelbetowe*, ed. Ireneusz Jóźwiak, Wojciech Biliński, Zbigniew Dzierżewicz, Zbysław Kałkowski, Janusz Krasnowski, Włodzimierz Starosolski, Zbigniew Walawski, Jan Wiśniowski, and Jan Witkowski, vol. 3 (Ustroń: Amgraf, 2002), 318.

[15] „Norcure® Re-Alkalization – Concrete Corrosion Repair", accessed February 16, 2018, https://www.vector-corrosion.com/norcure-re-alkalization.

[16] Mariusz Jaśniok and Adam Zybura, „O mechanizmach i trwałości zabiegu realkalizacji skarbonizowanego betonu", in *Kontra 2000 Trwałość budowli*, 133.

[17] Jaśniok and Zybura, „O mechanizmach", 134.

Ca^+ in pore solution move towards the reinforcement whereas anions OH^-, CO_3^{2-}, HCO_3^- – towards external anode mesh. Translocating of ions OH^- towards an external anode is an unfavorable phenomenon although it may be alleviated by alkaline cations migrating towards the reinforcement and by electro-osmotic flow.

To conduct the procedure well, electrical continuity of the reinforcement has to be provided. Electrical connection with the reinforcement can be made up in defected and loosen parts with bare reinforcement visible, so that damage would not deepen. Such method of providing connection was used by Italians during their conservation works over a monumental St Anthony's Church in Valmadrera, dating 1926, enlisted as part of Italian cultural heritage[18]. Realkalisation was conducted on eight columns topping a bell tower. Before starting work, the restorers measured how deep carbonation had gone, they had assessed thickness of covering and conducted electrochemical mensuration of reinforcing steel's potential and its polarity resistance. As an electrolyte, they used 1M and 0,5M of Na_2CO_3 solution, which is considered the best electrolyte as far as repassivation of steel is concerned[19]. During the seventeen-day-long process they were constantly monitoring reinforcing steel's potential and current density. The procedure succeeded[20].

Other examples of successfully conducted realkalisation of architectural monuments are the elevations of St Markus Church in Bettlach (Switzerland), St Marcel's Church in Paris, the Castle in Osaka (Japan), the building of Norwegian National Bank in Stavanger, Technical University in Trondheim or the Hoover Building in London – a monumental one built in art déco style, enlisted as an example of British cultural heritage[21]. In the case of Norwegian National Bank's facade, the authorities demanded the conservation to be conducted without breaching degraded yet historical concrete. Before works commenced, the examination had been conducted that revealed that as much as 70 percent of the reinforcement had been corroded. The proce-

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[18] Luca Bertolini, Maddalena Carsana, and Elena Redaelli, "Conservation of Historical Reinforced Concrete Structures Damaged by Carbonation Induced Corrosion by Means of Electrochemical Realkalisation", *Journal of Cultural Heritage* 9 (2008): 380, accessed June 20, 2012, doi:10.1016/j.culher.2008.01.006.

[19] Phil F. G. Banfill, "Re-alkalisation of Carbonated Concrete – Effect on Concrete Properties", *Construction and Building Materials* 4 (1997): 255–258, accessed September 19, 2010, doi:10.1016/S0950-0618(97)00045-7.

[20] Bertolini, Carsana, and Redaelli, "Conservation", 384.

[21] Zybura, *Zabezpieczanie*, 111–114.

dure of realkalisation that was chosen made it possible to restore passive reinforcement's condition and to maintain the original elevation of handly--grained concrete.

The drawback of electrochemical realkalisation is high cost of the procedure which requires complex machinery for electrochemical measurement. It also requires abundant drilling in order to maintain electrical continuity of the reinforcement. Furthermore, possibility of using this method is conditioned by specificity of construction. Diversification of external surface might appear to be a huge obstacle.

Regarding small-dimensional buildings with higher absorptivity and porosity of concrete, typical for most of artificial stone from the second half of the 19th century and from the 20th century, it is possible to conduct diffusive realkalisation there. This method also reflects well on pore solution's composition, reinstating high pH level, and has an impact on recreating an oxide film on the reinforcement. Diffusive realkalisation involves usage of highly alkaline solutions that imitate pore solution – to elevate pH level of concrete. The liquid is moved by the processes of capillary transportation, as well as by diffusion[22]. In case of smaller statues, it is possible to shorten the process by drying them and then soaking in a bath filled with solution. Regarding large statues – solution can be inserted by means of painting, spraying, continuous flow or, the most effectively, a vacuum conservation method. It is best to conduct it in the summer, after several weeks of sunny and dry weather. Solution can also be inserted by using a poultice of cellulose fiber, insulated with cling film for a few days, in order to have the solution inserted and to reduce water evaporation.

Diffusive realkalisation can be used not only in repassivation of reinforcement, but also much in advance – preventively, so that decline of passive condition will not occur[23]. Research shows that this method might prove to be as effective as traditional electrochemical realkalisation. Furthermore, it does not require using of expensive and complex apparatus for taking electrochemical mensuration[24]. After the procedure, concrete is able to reach pH level within limits of 12,5–13,5 and reinforcing steel is bound to undergo

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[22] Fernanda W. C. Araújo and Enio J. Pazini Figueiredo, "Realkalisation of the Carbonated Concrete Using Alkaline Solutions, *Quality of Structures and Advances in Materials* 229 (2005): 19–32, accessed August 23, 2010, https://www.concrete.org/store/productdetail.aspx?ItemID=SP229AP-%7c-14989&Format=DOWNLOAD&Language=English.

[23] Araújo and Figueiredo, "Realkalisation", 20.

[24] Araújo and Figueiredo, "Realkalisation", 21.

repassivation. Concrete becomes denser, therefore it is less absorptive and tends less to undergo re-carbonation[25].

Solutions used in realkalisation might have various composition: the most basic, i.e. saturated solution of calcium hydroxide or 1 M of sodium carbonate, mixtures of sodium carbonate, potassium hydroxide and sodium hydroxide solutions (in various concentration)[26] as well as an electrolyte with parameters closest to the composition of concrete's pore solution, being a mixture of solutions composed of three hydroxides: calcium, sodium and potassium[27]. Research has shown that best results could be achieved when using a mixture of sodium carbonate, potassium hydroxide and calcium hydroxide solutions. Sodium carbonate solutions are not suitable for the procedure because of the danger of salting out[28]. A presence of reactive aggregate is contraindication to perform the procedure. If the material contains reactive aggregate, realkalisation might contribute to a dangerous consequence – alkaline aggregate reaction[29]. Therefore, before proceeding with realkalisation, there should be petrographic testing conducted, in order to identify dangerous minerals.

Diffusive realkalisation was conducted by the author of this article while working on conservation of a cycle of busts (1971) by Jerzy Sobociński, the sculptor, in National Museum in Szreniawa[30], and the statue of Christ (1936) from the monumental St George's Cemetery in Toruń[31] (fig. 3, 4).

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[25] Banfill, "Re-alkalisation", 255–258.

[26] Araújo and Figueiredo, "Realkalisation", 26.

[27] Adam Zybura and Andrzej Śliwka, „O skuteczności zabezpieczenia przed korozją zbrojenia konstrukcji żelbetowych inhibitorami migrującymi", *Ochrona przed Korozją* 1 (2008): 4; Magdalena Klakočar-Ciepacz and Piotr Falewicz, „Poszukiwanie nowych mieszanek inhibitorów migrujących", in *Kontra 2002 Trwałość budowli*, 131.

[28] Araújo and Pazini Figueiredo, "Realkalisation", 21.

[29] A contraindication to perform realkalisation is the presence of reactive form of silica in an aggregate (hornets, silica limestones, riolites, dactyls, tuffs, andesites, gneisses and granites), as well as the presence of dolomites. Reactive forms of silica are opal, chalcedony, tridymite and cristobalite.

[30] Aleksandra Gralińska-Grubecka, „Dokumentacja prac konserwatorskich i restauratorskich popiersia Dezyderego Chłapowskiego" (restorer's documentation, Toruń 2012, Muzeum Narodowe Rolnictwa i Przemysłu Rolno-Spożywczego (later as: MNRPR-S) in Szreniawa); Aleksandra Gralińska-Grubecka, „Dokumentacja prac konserwatorskich i restauratorskich popiersia Daniela Janasza" (restorer's documentation, Toruń 2012, MNRPR-S in Szreniawa); Bartosz Paradowski under the supervision of Aleksandra Gralińska-Grubecka and Katarzyna Polak, „Dokumentacja prac konserwatorskich i restauratorskich popiersia Michała Drzymały" (restorer's documentation, Toruń 2016, MNRPR-S in Szreniawa).

[31] Barbara Ćwiklińska, Magdalena Firkowska, Justyna Korchut under the supervision of Aleksandra Gralińska-Grubecka and Anna Zaręba, „Nagrobek z betonowym przedstawieniem Chrystusa dźwigającego krzyż. Dokumentacja prac konserwatorskich i restauratorskich" (restorer's documentation, Toruń 2013, Towarzystwo Miłośników Torunia).

Fig. 3 and 4. The bust of Michał Drzymała by the sculptor Jerzy Sobociński (1971, National Muse-
              um of Agriculture and Agricultural and Food Industry in Szreniawa) and the statue
              of Christ from 1936 (St George's Cemetery in Toruń) are in a very good state of pres-
              ervation after realkalisation procedure. Photo by A. Gralińska-Grubecka

Before the decision of performing this procedure was taken, there had
been conducted petrographic research which had not confirmed presence of
dangerous components. In the case of Christ's statue, the solution was in-
serted by means of intensive, long-lasting painting, aiming at impregnating
it deeply. Furthermore, all of cracks present were injected with migrating
corrosion inhibitor (MCI). At the last stage of restoration works, in need to
minimize washing out of the realkalisating solution, the whole statue was
protected with hydrophobicizing impregnation.

In the case of busts, the sculptures had been dried before conducting the
procedure. Then they were cover with three-layered thick polyethylene film
(fig. 5). The sculptures were turned upside down and then filled with with
realkalisating solution, prepared immediately before impregnation and com-
posing of a mixture of three hydroxides: of potassium, sodium and calcium.
pH value of the mixture prepared was 13,11. After having impregnated the
sculptures entirely, the solution was removed, while the busts were left to
dry naturally (fig. 6).

Fig. 5. Dezydery Chłapowski's bust during the procedure of diffusive realkalisation. Photo by A. Gralińska-Grubecka

Fig 6. The bust drying out after the procedure of realkalisation had finished. Photo by A. Gralińska-Grubecka

An organoleptic examination with an unaided eye did not prove any signs of colour shift in sculptures. After the procedure, the pH level of an artificial stone was being controlled – it read 12,0 to 12,6 (desirable increase that was noted stretched from 0,56 to 0,82 depending on where the sample had been taken from). Six years have passed since the realkalisation procedures were conducted, and no reccurence of corrosion to the reinforcement has been observed. No loosening of the surface fragments of concrete has been observed either.

The above mentioned qualities and practical usage of diffusive realkalisation in conservation encourage to conduct deeper research in this field. In the research mentioned below, regularity of the procedure, pH increase and influence on a colour of impregnated material have been assessed.

Examination of realkalisation's regularity and its influence on pH increase

15 cuboid samples of carbonized concrete (size 5 x 5 x 6 cm), made at the beginning of the 40s., and two irregular fragments of historical mortar from the bust of Michał Drzymała (by Jerzy Sobociński, dating 1971, from National

Museum in Szreniawa), loosen as a result of corrosion, have undergone examination. To examine them, samples of the material have been taken from certain places (0–2 cm, 2–4 cm, 4–6 cm down, measured from the surface of the samples), in form of core drilling, 10 mm in diameter[32]. Immediately after the drilling had been finished, the procedure of preparing water extracts to measure pH level were started. The procedure of preparing extracts was conducted in accordance with PN-B-01807:1988 norm[33]. After its pH had been examined, the concrete was saturated during the process of bath in realkalisating solution. Basing on source literature and a consultation with Dr Ph. D. eng. A. Zybura, as a realkalising solution there was chosen a liquid closest in the composition to the composition of pore solution of non-carbonized concrete, with pH level of 13, consisting of[34]:

–1 part of volume 0,06 M KOH,

– 1 part of volume 0,2 M NaOH,

– 1 part of 0,001 M $Ca(OH)_2$.

After saturation, the samples were removed from the solution and left to dry freely in laboratory conditions. A part of cuboid samples was insulated with film, with an upper section of their surface left unprotected to enable water to evaporate (fig. 7). The appearance of the surface was being observed, especially the look of the unprotected upper part of evaporating (it was possible that hydroxides would migrate to the surface and an efflorescence would appear). After two months, pH level was examined again. Table no. 1 presents the results.

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[32] The drilling has been performed with a diamond core drill (Rubi company), 10 mm in diameter, in dry environment, using a low-speed driller. The drilling has had numerous breaks – to avoid significant temperature increase.

[33] According to the procedure of preparing water extract in order to establish pH level, a sample of concrete is to be crushed, seeds of thick aggregate are to be removed. Next, it should be ground in a mortar and sifted with 0,2 mm-eyelets sieve. The sifted powder should be inundated with distilled water in the following ratio: 1 part of powder and 10 parts of water (distilled water should have its pH = 6,0 ± 0,5 and its conductivity ⩽5 µS, measured in the temperature of 25 ± 5°C). The prepared mixture is to be extracted in the temperature of 25°C until the shift of a glass electrode's potential measured against a reference electrode is lower or equal to 4 mV/h (after having performed probationary tests it was established that extracting for 3 hours matches these criteria). PN-B-01807:1988. Anti-corrosion protection in construction. Concrete and reinforced concrete structures – Principles of diagnostics in construction.

[34] To prepare solutions, there were used hydroxides with purity level cz.d.a (purity fit to be analyzed; the name of a Polish norm) and destilled water with pH of 5,97.

Tab. 1. pH level increase in mortar and concrete after the procedure of realkalisation

Concrete samples	Depth of the concrete examined – layer	Solution absorptivity 20°C [%]	pH before realkalisation	pH after realkalisation	pH increase
From the bust	surface (0–2 cm) – evaporation area	7,89	11,65	11,92	0,27
	middle (2–4 cm)		12,27	12,61	0,34
	bottom (4–6 cm)		12,09	12,39	0,30
From the bust	surface (0–2 cm) – evaporation area	7,95	10,41	10,87	0,46
	middle (2–4 cm)		12,26	12,72	0,35
	bottom (4–6 cm)		11,80	12,32	0,52
From other objects	surface (0–2 cm) – evaporation area	5,41	11,10	11,47	0,37
	middle (2–4 cm)		11,53	11,87	0,34
	bottom (4–6 cm)		10,23	10,65	0,42
From other objects	surface (0–2 cm) – evaporation area	5,08	10,36	11,01	0,65
	middle (2–4 cm)		10,85	11,24	0,39
	bottom (4–6 cm)		10,86	11,37	0,51
From other objects	surface (0–2 cm) – evaporation area	5,29	10,27	11,09	0,82
	middle (2–4 cm)		11,29	11,94	0,65
	bottom (4–6 cm)		10,95	11,76	0,81
From other objects	surface (0–2 cm) – evaporation area	5,49	10,16	10,92	0,76
	middle (2–4 cm)		11,10	11,77	0,67
	bottom (4–6 cm)		10,76	11,56	0,80
From other objects	surface (0–2 cm) – evaporation area	5,18	10,21	10,85	0,64
	middle (2–4 cm)		11,20	11,82	0,62
	bottom (4–6 cm)		10,93	11,63	0,70
From other objects	surface (0–2 cm) – evaporation area	5,65	10,78	11,46	0,68
	middle (2–4 cm)		11,85	12,41	0,56
	bottom (4–6 cm)		10,90	11,57	0,67
From other objects	surface (0–2 cm) – evaporation area	5,84	10,37	11,05	0,68
	middle (2–4 cm)		11,43	12,13	0,70
	bottom (4–6 cm)		10,32	11,02	0,70
From other objects	surface (0–2 cm) – evaporation area	5,49	10,16	10,92	0,76
	middle (2–4 cm)		11,10	11,77	0,67
	bottom (4–6 cm)		10,76	11,56	0,80
From other objects	surface (0–2 cm) – evaporation area	5,18	10,21	10,85	0,64
	middle (2–4 cm)		11,20	11,82	0,62
	bottom (4–6 cm)		10,93	11,63	0,70
From other objects	surface (0–2 cm) – evaporation area	5,65	10,78	11,46	0,68
	middle (2–4 cm)		11,85	12,41	0,56
	bottom (4–6 cm)		10,90	11,57	0,67
From other objects	surface (0–2 cm) – evaporation area	5,84	10,37	11,05	0,68
	middle (2–4 cm)		11,43	12,13	0,70
	bottom (4–6 cm)		10,32	11,02	0,70
From other objects	surface (0–2 cm) – evaporation area	6,41	11,23	11,71	0,48
	middle (2–4 cm)		11,33	11,79	0,46
	bottom (4–6 cm)		10,32	10,84	0,52

Fig 7. Samples drying after the procedure of diffusive realkalisation. Photo by A. Gralińska-
-Grubecka

Among the results of diffusive realkalisation there have been observed: pH level increase in concrete and mortar within range of 0,27 to 0,82 pH units. The process of realkalisation went evenly within the whole volume of the material impregnated, migration of hydroxides to the surface while drying was not observed whatsoever.

Realkalisation's influence on colour shift of an artificial stone

In order to examine how the procedure had influenced a colour of an artificial stone, the samples of the mortar taken from Michał Drzymała's bust and the samples from other objects were cut out and they underwent an examination with the usage of colorimeter MiniScan XE Plus[35]. Following the examination, the samples were re-alkalised and examined again with a colorimeter after 12 months (tab. 1, fig. 8–11). That mensuration, as well as observation by an unaided eye, pointed out that realkalisation did not influence the colour of concrete examined. The chosen results representative for all 16 samples examined are presented below.

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[35] There was used a colorimeter MiniScan XE Plus by HunterLab The Color Managment Company.

Tab. 2. Mensuration of mortar' and concrete's colour before and after realkalisation, conducted with colorimeter

Concrete samples	dL[1]	da[2]	db[3]	DE[4]
From the bust	1,22	–0,67	–0,03	1,4
From other objects	0,61	0,36	0,54	0,89
From other objects	0,74	–0,12	–0,36	0,83
From other objects	1,06	–0,02	0,45	1,16

L – Cielab lightness range from 0 to 100,
dL[1] > 0 lightness increases,
dL[1] < 0 lightness decreases,
da[2] > 0 colour saturation increases towards red,
da[2] < 0 colour saturation increases towards green,
db[3] > 0 colour saturation increases towards yellow,
db[3] < 0 colour saturation increases towards blue.

$DE= \sqrt{(dL)^2 + (da)^2 + (db)^2}$

DE[4] 0–2 difference in colour unnoticeable
2–3 difference in colour noticeable for a trained eye
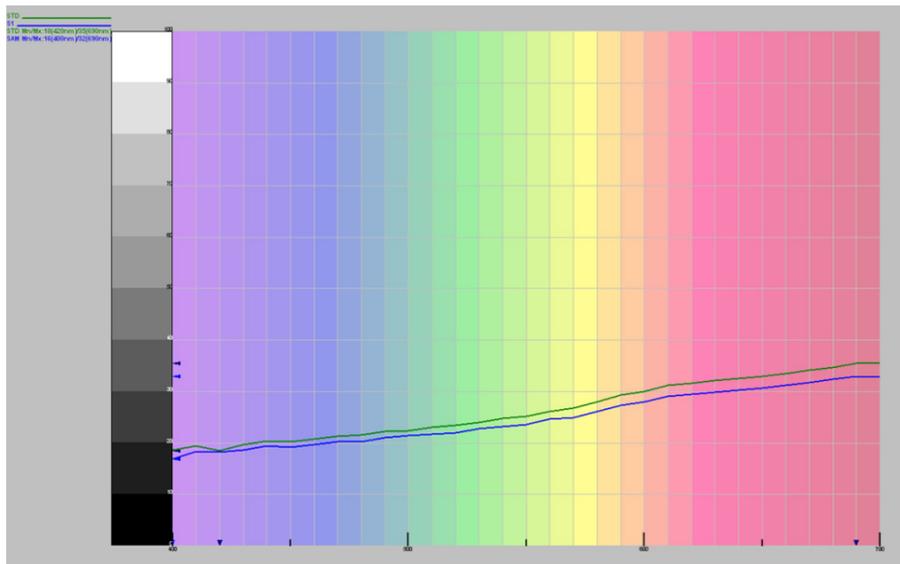more than 3 – difference in colour noticeable

Fig. 8. Mensuration of concrete's colour from the bust of Daniel Janasz before and after the procedure of realkalisation, conducted with colorimeter. Drawn by A. Gralińska-Grubecka
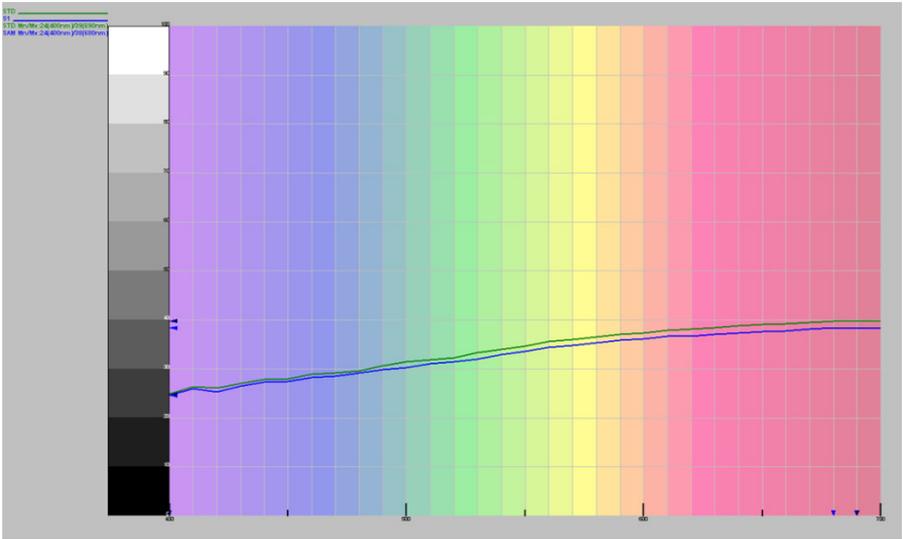
Fig. 9. Mensuration of concrete's colour in a sample from the beginning of the 40s before and after the procedure of realkalisation. Drawn by A. Gralińska-Grubecka
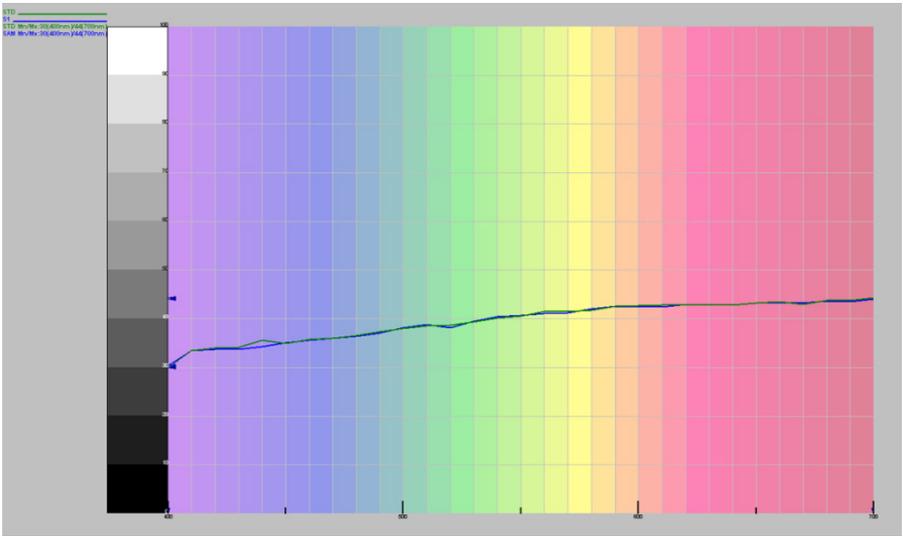

Fig. 10. Mensuration of concrete's colour in a sample from the beginning of the 40s before and after the procedure of realkalisation. Drawn by A. Gralińska-Grubecka
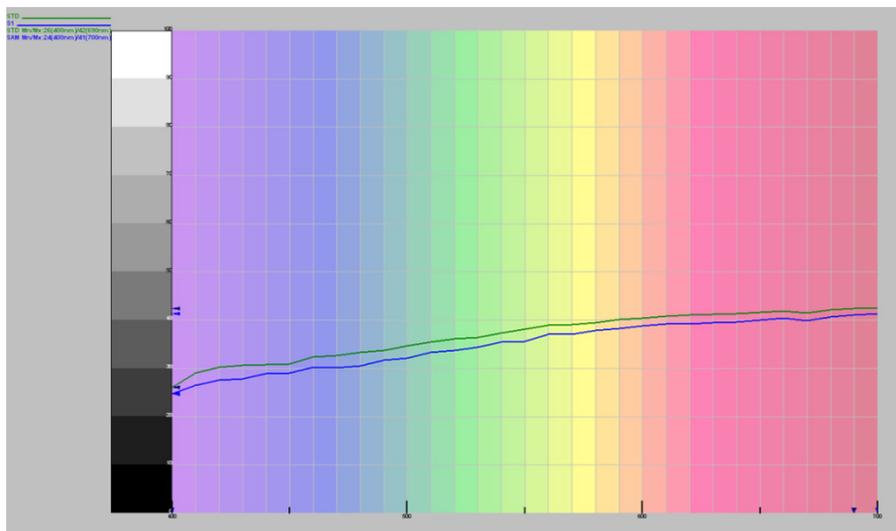
Fig. 11. Mensuration of concrete's colour in a sample from the beginning of the 40s before and after the procedure of realkalisation. Drawn by A. Gralińska-Grubecka

Conclusion

The research conducted over relatively poorly recognized method of diffusive realkalisation indicated its numerous qualities. Re-establishing high pH in order to limit corrosion of reinforcement was possible thanks to capillary and diffusive transport of highly alkaline solutions. This procedure might be conducted preventively, to not allow reinforcement's passivation to be lost. The mixture of hydroxides used in the procedures guaranteed increasing concrete's pH ranging from 0,27 to 0,82, depending, among other things, on absorptivity of an artificial stone which was undergoing realkalisation. The increase gained was relatively regular in the whole volume of material impregnated, there was no migration of compounds to the surface whilst drying, moreover the procedure have not affected colour shift of the samples treated. In case there is need to achieve a higher pH level, there can be used a liquid with higher concentration of hydroxides, e.g. with pH level of about 13,5.

In comparison to expensive electrochemical realkalisation that demands performing numerous drills in an object in order to establish electrical connection, diffusive realkalisation is a cheap and simple procedure, and does not demand causing additional damage to sculptures either.

A disadvantage of the method is the fact that it has to be limited to highly absorptive materials, and, in case of larger statues, there are difficulties inserting a solution evenly within all of their volume. Despite these drawbacks though, the advantages are noticeable and a positive result of the research is the encouraging factor to continue with the procedure of treatment.

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