A case study on corrosion conditions and guidelines for repair of a reinforced concrete chimney in industrial environment

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ABSTRACT

This paper presents a case study of corrosion damage of a concrete chimney sited in a steel production plant in front of the Mediterranean Sea. The aggressive environment to which the chimney is exposed and its limited accessibility make the assessment of its condition critical. Destructive and non-destructive tests have been carried out over time to evaluate possible deterioration phenomena of concrete and corrosion of the reinforcement. The available documentation both on the construction and on previous repair interventions, besides the results of several investigations are discussed in the paper with the aim of assessing the chimney and proposing guidelines for the design of a durable and effective repair intervention, in relation with reinforcement corrosion. Results show that it is not possible to identify a single cause of damage, but rather a synergistic effect of corrosion of steel reinforcement due to chlorides ingress and carbonation and a moderate chemical attack of concrete due to exposure to fumes of the plant. Moreover, although the chimney was repaired several times, such interventions, not properly realized, promoted corrosion rather than control it.

KEYWORDS

Reinforced concrete chimney; corrosion assessment; chlorides ingress; carbonation; industrial environment; inspection; repairs

1. Introduction

Some of the structures of steel production plants, such as, for example, chimneys, are realized in reinforced concrete. These structures are subject to the action of both the surrounding environmental condition and the aggressive substances with which they may be in contact due to the processes in progress inside the industrial plant. As far as their durability is concerned, it is well known that steel in sound concrete is initially protected by the alkalinity of concrete pore solution which promotes passivation of the steel (Bertolini, Elsener, Pedeferri, Redaelli, & Polder, 2013). However, experience has shown that corrosion is frequently the main cause of degradation of reinforced structures over time. It can take place when the passive film on steel surface is removed or is locally damaged due to carbonation of concrete or chloride penetration.

Figure 1 shows the typical evolution in time of degradation of reinforced concrete structures due to carbonation-induced corrosion (*black line*, *1*). In a first stage of the service life (*initiation phase*) the steel reinforcement is passive and no corrosion takes place. Carbonation, however, beginning from the concrete surface, penetrates the concrete cover so that the pH of the pore liquid decreases. Corrosion initiates when the carbonation front reaches the steel reinforcement and the passive film becomes unstable. The second phase is the *propagation of corrosion* that begins when the steel is depassivated and ends when a limiting state is reached beyond which consequences of corrosion cannot be further tolerated (Bertolini et al., 2013). The duration of the initiation phase depends on the concrete cover and the penetration rate of the CO_2 (that is influenced by several factors, mainly the concrete quality and concrete humidity). The situation might become much more severe if chlorides or other aggressive agents penetrate in the concrete (such as in marine and industrial sites).

Thus, the combined effect of chlorides, carbon dioxide (CO_2) and further aggressive agents could reduce the initiation time (Figure 1, *red line 2*). Moreover, the evaluation of the propagation phase with the possible limiting states could be quite complicated due to the large number of variables - including temperature and relative humidity - that could promote the kinetics of penetration processes of aggressive agents in concrete and accelerate corrosion propagation. In such cases, the prediction of residual life is prudently based on initiation time only.

The specific conditions to which some of the reinforced concrete structures present in industrial plants are exposed can make, therefore, the degradation phenomena more intense than that of conventional reinforced concrete structures in civil or construction field. Due to aging of reinforced concrete structures in existing steel production plants, the number of repair interventions on degraded structures is increasing. On the other hand, the need to ensure the continuity of the current production of steel and the efficiency of this type of process, requires extending the service life of existing plants (rather than re-design them) and, consequently, also that of the related reinforced concrete structures. However, the restoration of such structures might be complex both because in the past they were not

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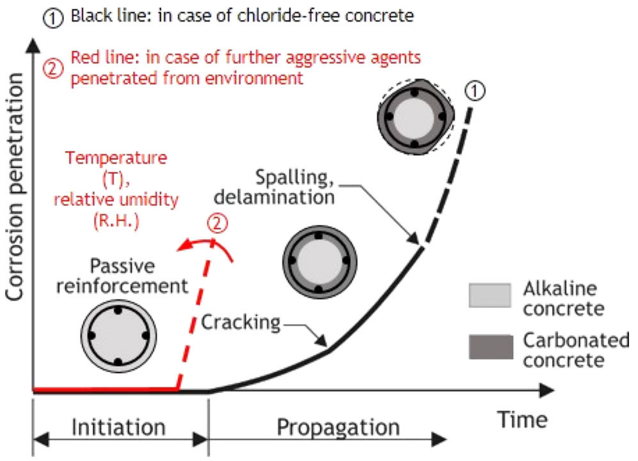


Figure 1. Evolution in time of the degradation due to corrosion (adaptation of Tuutti's diagram).

designed and maintained taking into account the actual exposure conditions to which they would have been exposed over time, but also because specific criteria and guidelines for repair are not available. In addition, often there are also execution difficulties related with the need to keep processes of the plants in progress.

Although in recent years many advances have been accomplished in the field of durability of reinforced concrete structures (Bertolini, 2008; Bertolini et al., 2013; COST Action 521, 2003), there is a need to promote further research in order to deepen practical aspects of assessment and monitoring of existing structures in industrial plant; at this regard, few papers are present in literature (Dan et al., 2010; Guo & Zhang, 2019; Maj, Ubysz, Hammadeh, & Askifi, 2019; Maj & Ubysz, 2018; Stoian et al., 2009; Wang & Fan, 2019). This paper aims at providing a contribution to improve that knowledge by presenting a case study on the diagnosis of deterioration and selection of repair for a reinforced concrete chimney sited in a steel production plant in front of the Mediterranean Sea. The chimney is 47 years old and it is currently in a condition of advanced deterioration, in spite of two previous repair interventions. Moreover, its limited accessibility could affect the repair intervention and make its execution critical. Destructive and non-destructive tests were carried out over time on the chimney; in particular, some cores have been recently sampled and analysed in order to evaluate the deterioration phenomena of concrete and corrosion of the reinforcement (aspects related with structural safety and stability are not considered here). The paper discusses the condition assessment of the chimney and it proposes guidelines for the design of repair intervention, in relation with reinforcement corrosion.

2. Case study

2.1. Description of the structure and previous repair interventions

Located inside a steel production plant, the chimney is made of reinforced concrete and it is 120 m high with a section that changes with the height (rounded octagonal up to a height of 30 m, with diameter ranging from about 9 m at the bottom to about 6 m at height of 30 m, and then constant up to the top). It releases fumes at temperature around 200 °C and it is internally coated with refractory bricks. The thickness of the concrete wall ranges between 360 mm at the bottom and 160 mm at the top. The chimney was built in 1972 and was subjected to several repair interventions during less than 50 years of service. Table 1 summarizes the repair interventions made on the chimney over time by indicating the year in which they were carried out and the relative portions of chimney subjected to them.

Generally, the interventions consisted of a partial scarifying of concrete of the chimney and the laying of repair cementitious materials through spray technique. A first repair intervention was carried out in 2002 (30 years after the construction), followed by another one in 2012 (only 10 years after the previous one). Even more limited duration of the latter intervention than the former is confirmed by evidences of degradation which have been recently documented (June-July 2019) in the zones of the previous repair interventions. No data on composition and properties both of concrete and steel used for the chimney construction were provided.

2.2. Evaluation procedure

The chimney was subjected over time to several diagnostic investigation campaigns (Table 1). The first one dates back to 1999; neither the reason that led to the investigations nor the location of the samples was specified (only the height at which they were taken: between 35 m and 57 m). The next one was made in 2002, following the damages found on the South side of the chimney at heights between 25 m and 65 m as a support to the intervention carried out in the same year. An inspection campaign was carried out also in 2007 in order to assess the conditions of the chimney after only 5 years from the previous intervention. Finally, another investigation was done in 2019 in view of a new repair intervention.

During the several inspections some visual observations of the structure were carried out to assess the signs of deterioration and to locate zones for sampling (Figure 2(a)–(b)). Phenolphthalein test was carried out on concrete samples to assess the depth of carbonation; moreover, both chloride and sulphate contents were measured on samples collected at different depths. Measurements of density, water content and compressive strength were also carried out on two cores collected during the last inspection in zones $A1$ and $A2$ (Figure 2(c)). These samples, named respectively $A1$ and $A2$, allow to understand the stratigraphy of the cementitious materials used to realize and repair the external wall of the chimney. Core $A2$ is made up of a concrete portion and an overlying coating of mortar. Differently, core $A1$ is homogeneous and is characterized only by concrete.

Chemical and thermo-gravimetric analyses (TGA) were performed on such samples, as well as some microstructural analyses by means of scanning electron microscopy (SEM)

Table 1. Summary of interventions of repair and inspection carried out on the chimney.

						Type tests: *Mechanical*	*Physical*		*Chemical*				*Micro*		
Intervention	*Year*	*Side*	*Height (m)*	*Sample number^*	*Type Sample*	*R*	*D*	*A*	*Cl*	*SO$_4$*	*TGA*	*C^, pH*	*S*	*E*	*X*
Inspection	1999	–	35–57*	3	C	V	V	V	V	V	–	V	–	–	–
Repair/Inspection	2002	*S, N*	18–75* 25–65* 25–67*	not specified (*N, S*)	C, S	V	V	V	V	V	–	–	–	–	–
Inspection	2007	*S, N*	–	9(*S*), 5(*N*)	C, M	V	V	V	V	V	–	V °	–	–	–
Repair	2012	*S*	20–75	–	–	–	–	–	–	–	–	–	–	–	–
Inspection	2019	*S*	20–45*	2(*S*)	C, M, S	–	V	V	V	V	V	V °	V	V	V

Legend: exposure *side of chimney* (*S*, south; *N*, north), *type of sample* (*M*, mortar; *C*, concrete, *S*, steel), *type of analysis*: *R*, compressive strength, *D*, density, *A*, water absorption, Cl, chlorides content, SO$_4$, sulphates content, *C*, carbonation depth, pH, pH measurement, *S*, SEM observation, *E*, EDS analysis, *X*, XRD analysis. TGA, thermo-gravimetric analysis. ^is referred to only cementitious samples: mortar or concrete (number and type of metallic samples are never specified; few observations are present in the available documentation). *Heights of chimney where inspection actions were made.

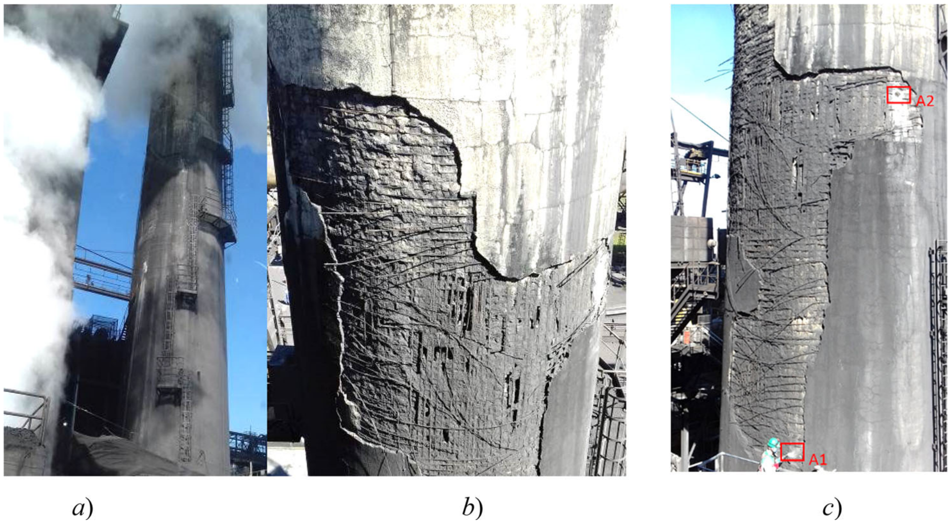


Figure 2. Exposure conditions of the chimney (a) and visual inspection carried out (b–c) in June-July 2019 (red rectangles indicate in Figure 2(c) the sampling zones *A1* and *A2*).

and optical microscopy and X-rays diffraction (XRD). All analyses were carried out by external laboratories and made available by the owner of the plant. The number and the type of samples collected from the structure during the various interventions of repair or inspection and the main analyses to which they were subjected are summarized in Table 1. In addition, analyses on the fumes of the plant were made during the last inspection in order to evaluate in detail the exposure conditions.

Table 2. Analysis of the pollutants emitted by the tower of the coke extinguishing unit, carried out in 2019 (*maximum content detected during the test).

Pollutans	*Compounds*	*Unit*	*Results*
Particulate phase	Powder	mg/m^3	20.2
	Ca	mg/m^3	0.49
	HF	mg/m^3	0.0725
Aerosol and gas	HF	mg/m^3	0.22
	SO$_2$	mg/m^3	53.6
	H$_2$S	mg/m^3	0.395
	H$_2$SO$_4$	mg/m^3	97.2
	NH$_3$	mg/m^3	7.9
	HCl	mg/m^3	2.22
	CO$_2$*	%	0.6
	CO*	mg/m^3	9200
	NOx*	mg/m^3	16
Condensate analysis	pH		6.2
	H$_2$S	µg/l	<200
	NH$_3$	mg/l	<0.1
	HF	mg/l	0.88

2.3. Environmental conditions

The chimney is exposed to an environment of marine-industrial type. Moreover, every 8 minutes it is invested by fumes coming from the nearby tower of the coke extinguishing unit (TEX) in case of wind coming from South (Figure 2(a)). The analysis of such fumes shows a high content of powders and a very high concentration of pollutants in form of gas and aerosol (among which chlorides, sulphur oxides, SO$_2$ and SO$_3$, nitrogen oxides, NO$_x$, ammonia, NH$_3$ and carbon dioxide, CO$_2$, Table 2). In particular, about 54 mg/m^3 of SO$_2$, 16 mg/m^3 of NO$_x$, 7.9 mg/m^3 of NH$_3$, 9200 mg/m^3 of CO and 0.6% of CO$_2$ are found; these concentrations are one or two order of magnitude higher than those reported in literature for an industrial environment (EN 206, 2013; ISO 9223:2012, 2012; Shreir, Jarman, & Burstein, 2000).

According to the classification of the European standard EN 206 (2013) the analyses of the fumes of the plant show that the chimney is exposed to classes *XC4* and *XS1*, respectively for the risk of carbonation in presence

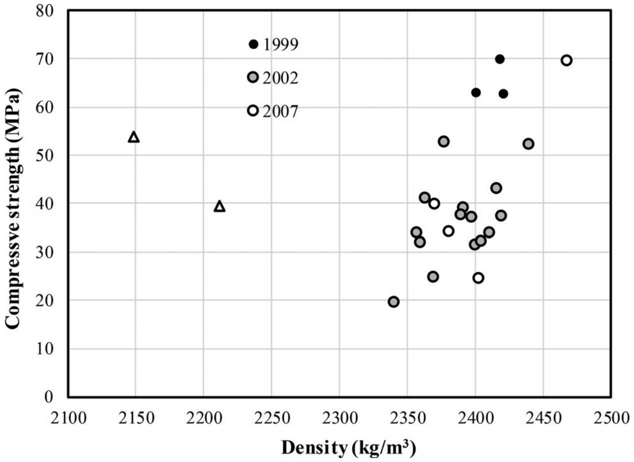


Figure 3. Values of compressive strength and density obtained on cores taken in 1999, 2002 and 2007 (triangles indicate values obtained on repair material).

of wet and dry cycles and of chlorides penetration being near to the Sea coast. In addition, the fumes of TEX and their condensates make the exposure locally more aggressive (Pavlik, Bajza, Rousekova, Uncik, & Dubik, 2007; Pedeferri, 2018). In fact, having high temperature (about 80–100 °C) the fumes contribute to create on the chimney surface a microclimate characterized by high humidity and temperature, besides high quantity of dust and pollutants. Moreover, concentrations of acids in the fumes (such as sulphuric acid (H_2SO_4), hydrofluoric acid (HF), hydrogen sulphide acid (H_2S) and hydrochloric (HCl)) are also extremely high (ISO 9223:2012, 2012; Pedeferri, 2018; Shreir et al., 2000).

However, the analyses made on the condensate (Table 2) have shown a pH slightly acid, with a value of 6.2, besides a negligible concentration of the pollutants. The condensate has a content of H_2SO_4 less than 0.1 mg/l; this concentration causes a content of SO_4^{2-} in condensed water next to the threshold identified by exposure class X*A1* as representative of a weakly aggressive environment according to EN 206. This exposure class is also confirmed based on the value of aggressive CO_2 measured in the condensate sample (15.4 mg/l); indeed, an exposure class *XA*1 is considered when aggressive CO_2 ranges between 15 mg/l and 30 mg/l.

3. Diagnosis of damage mechanisms

The inspection made in 2019 has documented wide detachments of cementitious material and severe corrosion of the reinforcements at heights between 20 m and 45 m. As in the past, the recent zones of degradation are facing South and are exposed leeward with respect to the cyclic action of the fumes of TEX (Figure 2(a)). Differently, concrete below the repair material (probably the original concrete) seems to have good mechanical performance. The following sections will concern the degradation phenomena of cementitious materials, steel corrosion and their role on the current condition of the chimney.

3.1. Degradation of concrete and repair materials

Concerning the characterization of original concrete, compressive strength tests have shown a decrease in time of mechanical performance (Figure 3). The investigation of 1999 had documented compressive strengths ranging between 62.7 MPa and 69.9 MPa; thus, such values were in accordance with ACI 307-98 which requires a specified concrete compressive strength not less than 20 MPa for reinforced concrete chimneys shall (ACI 307-98, 1988). Moreover, a density around 2400 kg/m^3 and a porosity between 8.3% and 11.4% were obtained. Based on the tests carried out in 2002 along the South side, concrete showed a reduced compressive strength which varied between 19.6 MPa and 52.8 MPa, while the density was comparable (2340–2439 kg/m^3).

The investigation of 2007 confirmed again a wide variability of the results. The significant mechanical resistance found initially for the concrete is compatible with a water/cement ratio (*w*/*c*) estimated equal to 0.47 and a supposed type of cement (CEM V) evaluated on the basis of recent thermo-gravimetric and chemical analyses made on samples of original concrete collected from zone *A*1 (Table 3). Microstructural observations carried out on concrete show the presence of several micro-cracks in the cement paste to which both the decrease of mechanical resistance in time and the wide variability of the results could be attributed. Moreover, based on the visual observations of cores, in particular those collected during the first investigations, the presence of macro-cracks which extended along the concrete wall of chimney emerged already since 1999, before the repair interventions. These discontinuities extended to a depth of about 60 mm, i.e., near the steel reinforcements. The formation of these cracks could be traced back to the settlement of the concrete which can crack right at the reinforcements after laying. This hypothesis might be confirmed by the presence of carbonated concrete at the depth of the reinforcements. The presence of such cracks was noticed in various concrete cores at a comparable depth.

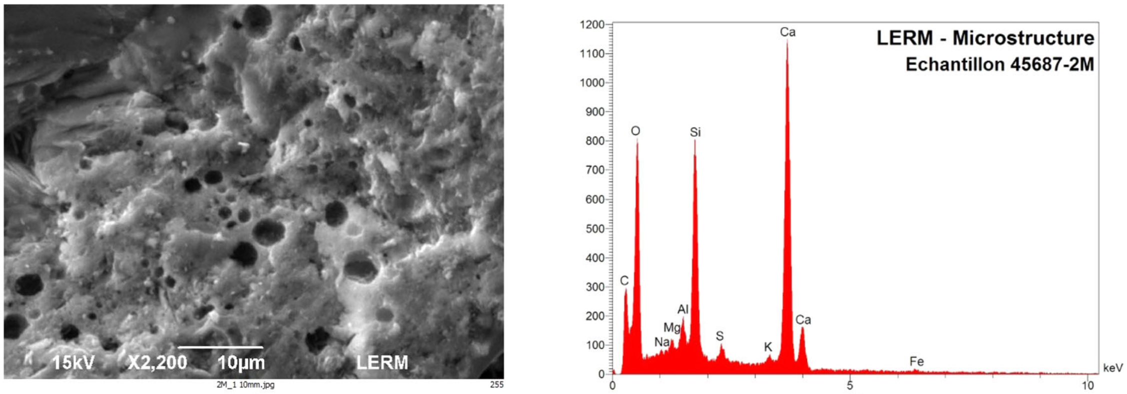
On the other hand, the repair materials used in the different interventions were not sufficiently characterized in terms of mechanical performance (triangle symbols in Figure 3); however, if properly placed, they should have guaranteed, in agreement with their technical datasheets, good mechanical and durability properties (for example, in terms of expansion, resistance to vapour diffusion and penetration of carbonation).

Indeed, recent investigations made on repair material used in the intervention of 2012 state that this material is a mortar with low water/cement ratio (w/c equal to 0.23–0.28) and with a cement dosage (type CEM I, with ground granulated blast furnace slag) equal to 620 ± 60 kg/m^3 (Table 3, repair mortar sample A*2*). Microstructural analysis confirms the cementitious nature of repair mortar sample. Its cement matrix consists of portlandite, calcium silicates hydrates and compounds based on calcium sulphate (Figure 4(b)). The widespread presence of carbon is also identified in depth (Figure 4(b)). In particular, the micrograph shows an amorphous carbonaceous compound which appears to be

Table 3 Summary of results of physico-chemical analyses and of observations made by optical microscopy on samples collected from chimney during the inspection carried out in 2019.

Properties	Unit of measure	Type of analysis	Sample *A*1	Sample *A*2	
			Concrete	Concrete	Repair mortar
Carbonation thickness	(mm)	*C*	3	> 50	0
Absolute density	(kg/m^3)	*M*	2470	2490	2145
Apparent density	(kg/m^3)	*M*	2350	2380	2050
Open porosity	(%)	*M*	12.3	10.7	9.3
Type of aggregate	–	*OM*	Calcareous	Calcareous	Siliceous
Type of cement	–	*OM* (*)	CEM II/A-V (6–10% fly ash)	CEM II/A-V (6–10% fly ash)	CEM I (<5% blast furnace)
SiO_2 soluble	(%)	*CH*	2.20	3.29	6.33
Al_2O_3 soluble	(%)	*CH*	1.21	1.16	1.26
Residue insoluble	(%)	*CH*	2.56	0.58	63.44
Free water (<80 °C)	(%)	*TGA*	0.3	0.4	0.5
Bonding water (80–630 °C)	(%)	*TGA*	4.2	4.1	5.5
Losses (630–1000 °C)	(%)	*TGA*	35.7	35.4	3.5
Total losses	(%)		40.2	39.9	9.5
Of which CO_2 from $CaCO_3$	(%)	*TGA*	35.5	35.2	3.2
For which: $CaCO_3$	(%)	*TGA*	80.7	80.0	7.3
Cement dosage	(kg/m^3)	Obtained^	355 ± 35	345 ± 35	620 ± 60
Water dosage	(kg/m^3)	Obtained^	150	145	155
water/cement (*w/c*)	–	Obtained^	0.42 (0.38–0.47)	0.42 (0.38–0.47)	0.25 (0.23–0.28)
Na_2O (40–60 mm)	(%)	*SEP*	0.11	–	
K_2O (40–60 mm)	(%)	*SEP*	0.06	–	–
Na_2O_{eq} (40–60 mm)	(%)	Obtained^^	0.15	–	–
Na_2O_{eq}** (40–60 mm)	(kg/m^3)	Obtained**	3.5	–	–

Type of analysis: *C*, phenolphthalein test; *M*, measurements of mass; *OM*, optical microscopy and petrographic analyses on thin sections (*); *CH*, chemical analysis; *TGA*, thermos-gravimetric analysis; SEP, plasma emission spectrometry. ^values obtained through elaboration of chemical (CH) and thermos-gravimetric analyses (TGA). **value obtained based on apparent density. ^^Na_2O_{eq} calculated as $Na_2O + 0.658\,K_2O$.



a) *b)*

Figure 4. Scanning electron microscope observation (a) and related EDS analysis (b) of the repair mortar sample *A*2 (LERM SETEC, 2019).

spread on the surface (Figure 4(a)) thus confirming the likely effect of atmosphere contaminants.

Nevertheless, despite promising features in terms of estimated water/cement ratio of this repair material, its cement paste appears to consist of small vacuoles and micro-porosities (Figure 4(a)) which favour the permeability to aggressive agents.

As a matter of fact, regarding the current condition assessment of the chimney, it is possible to distinguish wide delaminated zones, in which the repair material appears already strongly degraded and detached (Figure 5), from those macroscopically intact where the repair material shows superficial cracks with random distribution (Figure 2(b)). These superficial cracks could be the sign of stresses induced by drying shrinkage due to inappropriate execution or to a poor curing of the repair material. In particular, it should be highlighted that the spray technique used for the placement of the repair mortar is not considered adequate for such high thicknesses (higher than 50 mm). Moreover, once placed, the repair material has to be stable until setting and needs adequate curing; very likely the exposure condition might have made the curing step of repair material critical.

In any case, by excluding a predominant role of an early degradation, for instance caused by construction errors made in phase of implementation of repair mortar whose effects had to manifest prematurely, it remains to consider the effect of critical exposure conditions of the chimney and consequently the risks of degradation due to chemical reactions. Indeed, in an aggressive environment as that to which the chimney is exposed, both concrete, initially, and repair materials subsequently placed above it, may have undergone the penetration of aggressive agents in time (Bertolini et al., 2013; Collepardi, 2006; Coppola, 2007; Neville, 2011).

Sulphates in concrete may be due both to the gypsum present in the cement as regulator of setting time and to the

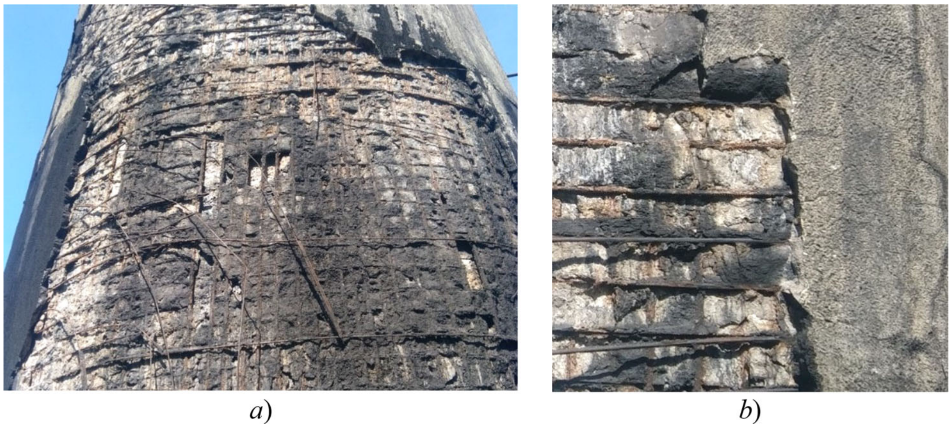

a) b)

Figure 5. Details of degradation of repair material (a) and corrosion reinforcement (b) of the chimney (documented in June 2019).

possible penetration of sulphate ions (for example, those dissolved in the fumes condensate) which can produce expansion effects when reacting with the constituents of cement matrix. In particular, different destructive reactions due to sulphates penetration in concrete could develop gypsum bi-hydrate ($CaSO_4 \cdot 2H_2O$), ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) or thaumasite ($CaCO_3 \cdot CaSO_4 \cdot CaSiO_3 \cdot 15H_2O$). The formation of thaumasite (Collepardi, 2006; Coppola, 2007; Neville, 2011), whose effects would have been more devastating, can be excluded considering that the fumes, although having high humidity and contaminants, are characterized by a high temperature which is not compatible with this specific reaction. Indeed, thaumasite develops in cold climate (0–5 °C) and wet environments (R.H.> 95%) rich of carbon dioxide.

The condensate formed on the concrete wall of the chimney has a content of H_2SO_4 less than 0.1 mg/l which can be associated with a weak attack degree (XS1, EN 206) for which no particular precaution is suggested in terms of type of cement and water/cement ratio (*w*/*c*) according to standard 201 ACI defined for sulphate-resistant concrete (Coppola, 2007). In fact, the sulphate content measured in depth on samples (internal side, *int*) of original concrete (i.e., on the portion close to the internal refractory layer) collected during the investigations of 1999 is equal to 3.8% by mass of cement (Figure 6(a)), lower than 5% expected in cement itself as setting time regulator. Values slightly higher (5.25–5.51% by mass of cement, Figure 6(a)) are measured only on the external faces of these samples (i.e., the portions close to the external surface of the chimney); however, these values are not sufficient to define pathological conditions.

The results of analyses carried out in 2007 (not reported in this paper) were mainly concerning the repair material in which the presence of sulphates was even lower than that of the previous analyses (Figure 6(a)). Recent tests (Figure 7(a)) show negligible values of sulphates in the repair mortar A*2*. In the original concrete the sulphates content measured during the last analyses is higher than the threshold value only in the outer 20 mm (6.29% by cement mass, Figure 7(a)). Indeed, analyses made by electron scanning microscopy show the presence of compounds based on calcium sulphate and monosulphate hydrates, especially in the outer 15 mm. In general, such concentrations are not considered significant to confirm that a sulphate attack is in progress, also because they are limited only at surface layer of original concrete. Moreover, the results obtained also through thermo-gravimetric analysis (*TGA*, Table 3) do not highlight significant differences between samples of repair mortar and those of original concrete.

Nonetheless, other expansive reactions can be responsible for the observed cracks (Neville, 2011) and detachment phenomena previously documented. Based on the analyses made, the available documentation does not mention any sign attributable to alkali-silica reaction. This degradation form can be excluded for negligible alkali content (Na_2O and K_2O) measured in concrete (Table 3). In addition, the observations carried out both with scanning electron and optical microscopy does not detect the presence of reactive aggregates in any sample of cementitious material.

Since cementitious materials have initially an alkaline pH, they are not particularly resistant to strong acids or compounds that can convert in acid. Concrete can be attacked by liquid with a pH value below 6.5 but the attack is severe only at pH below 5.5; below 4.5, the attack is very severe (Zivica & Bajza, 2001, 2002). The attack progresses at a rate approximately proportional to the square root of time because the phenomenon depends not only on pH but also on the solubility of salt formed after dissolution of the compounds of cement paste and the nature of its ions. Thus, the pH is not the only parameter indicative of the degree of the attack. Also, the presence of CO_2 shall influence the phenomenon, as well as the temperature of the fumes and the frequency with which they arrive on the chimney. Nonetheless, the documentation of the investigations made in 2002 highlights a substantial presence of concrete defined as "disintegrated" (for a thickness between 80 mm and 120 mm); this term could be traced back to the effects of the acid attack.

During the subsequent investigations, no considerations of the cohesion of cementitious materials were documented, except for those of 2019. In particular, microstructural analyses made in 2019 (Table 4) highlighted the good cohesion both of the cement paste of original concrete and of repair mortar. Only a superficial alteration (no more than 15 mm, Table 4) allows to confirm both the limited aggressiveness of the environment (*XA1*) in terms of acid attack and the

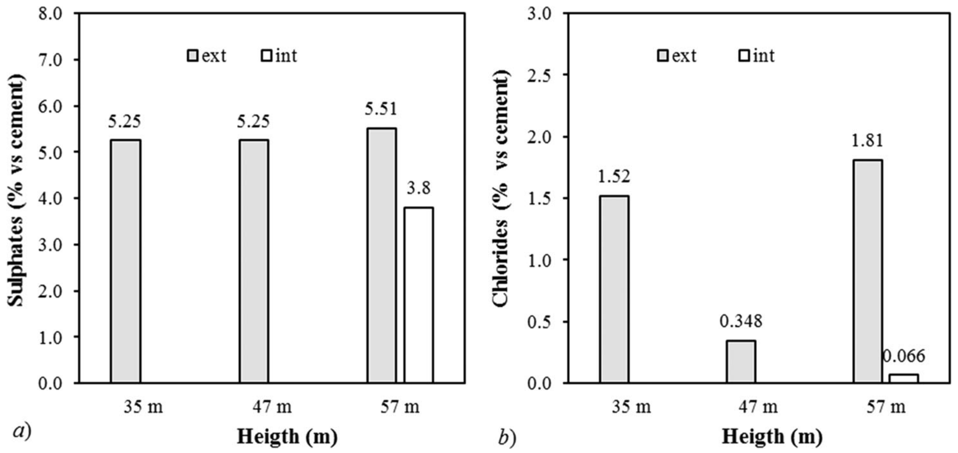


Figure 6. Results of sulphates (a) and chlorides (b) analyses on the external (*ext*) and internal (*int*) sides of concrete cores taken from the chimney in June 1999.

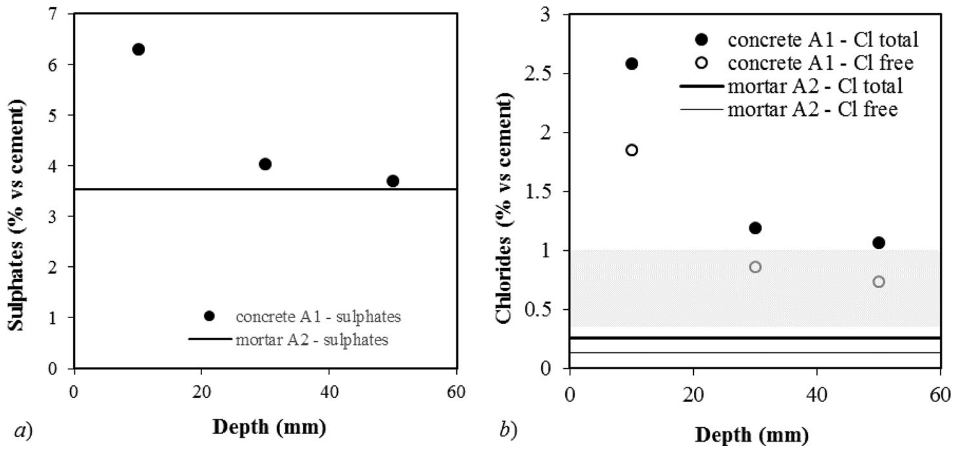


Figure 7. Sulphates (a) and chlorides (b, free and total) concentration as a function of depth for the concrete sample *A*1 taken in 2019. Grey background is indicative of the critical range of chlorides 0.4-1% by cement mass (in Figure 7(b)). The average contents measured in terms of sulphates and chlorides on the mortar sample *A*2 are also reported (black line).

Table 4. Summary of compounds and morphological characteristics detected by scanning electron microscope observations. Results obtained on cores *A*1 and *A*2 taken in 2019.

Materials	Sample name	Position	*Portlandite*	*Calcium hydrate silicate*	*Ettringite*	*Carbonaceous compounds*	*Sulphate compounds Ca/Mg*	Cohesion Microstructure observations
Concrete	*A*1	Surface	–	V	–	V	V	Alteration (20 mm)
		Deep	V	V	V	–	V	Good^
Repair mortar	*A*2	Surface	V	V	–	V	V	Alteration (20 mm)
		Deep	V[a]	V	V	V	V	Good
Concrete	A2	Surface	–	V	V	–	V	Good^
		Deep	V	V	–	–	V	Good^

(^presence of microcracks and [a]presence of amorphous coating, associated with carbon residues)

moderate resistance offered by the mortar itself. As far as the current degradation conditions of the wall of the chimney are concerned, wide and evident detachments are due not only to concrete deterioration, but also to reinforcement corrosion.

3.2. Reinforcement corrosion

The exposure conditions to whom the reinforcements of the chimney is subjected are particularly severe because of higher concentration of carbon dioxide in atmosphere (around 0.6%, Table 2) if compared to that of urban or rural environment (Bertolini et al., 2013; Pedeferri, 2018; Shreir et al., 2000). To evaluate the progress of carbonation suffered from the concrete of chimney, the results obtained in the several investigations have been analysed by considering the typical square root relationship used to describe the penetration of carbonation depth: $c = K \cdot t^{1/2}$, where c is the carbonation depth at certain time t (measured from the construction of the chimney) and K is the carbonation coefficient.

After 27 years, negligible carbonation thicknesses were measured (only 5–10 mm from cores collected in 1999). A

Figure 8. Visual observations of some reinforcement samples (LERM SETEC, 2019).

carbonation coefficient K ranging between 0.96 mm/year$^{1/2}$ and 1.92 mm/year$^{1/2}$ can be obtained. It is representative of a good concrete and/or of a wet environment that decreases the carbonation rate. Based on the estimated carbonation coefficient, a carbonation thickness of 6.6–13.2 mm should have been expected to be measured on the original concrete during the last investigation in 2019 (i.e., after 47 years of exposure at the same atmosphere and exposure conditions). With such carbonation thickness, lower than concrete cover (equal to 50–60 mm according to project prescriptions), the passive conditions should have been guaranteed for the reinforcements.

Nevertheless, the recent measurements have shown carbonation thickness ranging between a minimum of 3 mm and a maximum of at least 50 mm (Table 3); such carbonation thicknesses, also confirmed by measurements obtained in 2007, can indicate the following different situations:

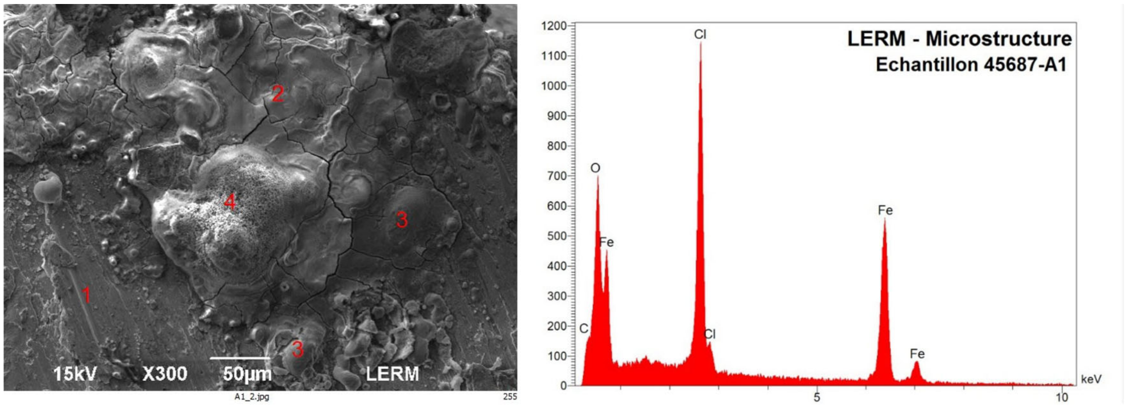
- zones where original carbonated concrete was completely removed and the overlying repair mortar (in general, not carbonated) has exerted a relevant protection function;
- zones where original concrete was not completely removed and the presence of cracks inside it have made it even more susceptible to carbonation progress.

However, in the detachment zones the reinforcements are visible (Figure 5(b)) and are in advanced state of corrosion with corrosion products that completely cover the segments of reinforcements taken in the zone $A1$ (Figure 8). Moreover, in these zones the bars often appear congested (Figure 2(b)); this may have prevented an adequate protection by concrete. Certainly, the maximum carbonation thickness measured on concrete in the last investigation campaign is comparable with that of concrete cover by confirming that not all steel bars are in passive condition. In addition, the presence of condensate on the external surface of the chimney increases the duration of periods of wetting. This may increase the rate of attack of the reinforcements that are already corroding. The temperature of fumes as well as the presence of various contaminants could also favour the kinetic of the phenomenon. In the case of the chimney, the wide detachments that have been documented may have been favoured, initially, by a poor adhesion between repair mortar and underlying concrete (probably for errors made during the placement of the cementitious materials or for an inadequate curing) while later for the carbonation progress up to steel bars depth.

In addition, the chimney is exposed to a marine environment (*XS1*); thus, the corrosion of steel bars might also be initiated due to the penetration of chlorides. In fact, during the investigation campaign of 1999, some samples were collected in order to analyses the chloride content. Therefore, it is reasonable to assume that the chimney already presented at that time signs of degradation attributable to corrosion of steel bars. The analyses of chloride content were carried out both on internal side of cores collected from concrete wall of chimney (i.e. close to the layer of refractory) and on the outer side (i.e. near to external surface of chimney) at different heights (Table 1).

The average chloride content on external side of cores is higher than the maximum of critical threshold range (0.4–1% by mass of cement for carbon steel) with values of 1.52–1.81% by mass of cement; conversely, a negligible chloride content is measured in depth (0.066% by mass of cement, Figure 6(b)). Differently, the analyses carried out after the first intervention (2007), probably on the repair materials applied along the South side of the chimney in partial replacement of the original concrete, showed that the chloride content was 0.25–0.56% by mass of cement, i.e., next to the lowest limit of critical threshold. Recent analyses showed that the presence of chlorides decreases with the depth (Figure 6(b)). However, even at depth of 50 mm a total chloride content higher than maximum limit of critical chloride threshold was measured.

Actually, EDS analysis has allowed to detect the presence of chlorine on the metal surface (Figure 9(b)) as well as to observe the morphology of its corrosion products (Figure 9*a*). Since the corrosion attack involves a large area of the reinforced segments (Figure 8), the morphology of pitting is not so evident, even if EDS analysis has confirmed the presence of chloride at the depth of steel surface. Differently, the analysis carried out during the same survey on a repair mortar sample shows a chloride content equal to 0.26% by mass of cement to be considered overall on a maximum thickness of 60 mm. Thus, the repair mortar shows a good resistance to chlorides penetration. On the other hand, the documented permanence in the original concrete of chlorides, in quantities certainly not negligible even at depths of 50 mm, represents a risk for the corrosion initiation. This confirms that the repair interventions on the chimney have not implied an appropriate removal of concrete contaminated by chlorides. Nonetheless, in the presence of chlorides at the cover depth, it is necessary to expect that in a carbonated concrete the corrosion rate of carbon steel bars can be high even for low relative humidity. In absence of complete removal of chloride-contaminated concrete, it would be useless to use a repair mortar with a certain resistance to



a)　*b*)

Figure 9. An example of SEM observation (a) and EDS analysis (b) carried out on steel sample (LERM SETEC, 2019).

the chloride penetration since chloride would continue to be present and act in depth.

Moreover, condition assessment of chimney has to take into account the fact that currently, following the wide detachments of concrete and repair mortar for restoration, parts of the reinforcements are no longer embedded (Figure 5); thus, they are directly exposed to atmosphere. In addition, the fumes that invest the chimney could represent a criticality also for the reinforcements currently exposed to atmosphere. However, it is necessary to highlight that the steel bars directly exposed to the atmosphere represent a transitory situation (before a planned intervention) and that the best way to protect them from corrosion is to embed them in an alkaline and chloride-free cementitious material.

4. Guidelines for the repair intervention

In its present condition, the chimney requires an urgent intervention aimed at repairing deterioration phenomena related with materials degradation. In this section guidelines for the design and execution will be provided with the aim to achieve the desired service life. Principles and aims of the repair are outlined according to RILEM 124-SRC recommendations (RILEM Technical Committee 124-SRC, 1994; Bertolini et al., 2013; COST Action 521, 2003).

The deterioration phenomena of the chimney are due to various factors that can be summarised as follows:

- high environmental aggressiveness, related to both the macroclimate of the industrial-marine environment of the steel production plant and the microclimate produced on the South side of the chimney by the contact with the extinguishing fumes of the TEX and their condensate;
- combined effect of carbonation and chloride-induced corrosion of reinforcement;
- mild chemical attack of concrete, unlikely to produce relevant deterioration by itself, that however exerted a synergistic effect with corrosion-induced deterioration, increasing and accelerating its consequences;
- repair interventions that were not effective in restoring durable protection of reinforcement due to incorrect design and execution, in particular with respect to the incomplete removal of non-protective concrete and unsuitable application and curing of repair material.

The first step for a repair intervention is the definition of the expected service life, i.e. the time during which no further intervention of extraordinary maintenance will be necessary. The service life is chosen by the owner with the support of the designer, and it is based on factors such as plant operation, scheduled maintenance, accessibility, economical aspects. In this case, the expected service life of the repair is 10 years. Then, it is convenient to define representative zones, which are homogeneous with respect to materials, exposure conditions and previous repairs. The chimney can be divided in three zones:

- the South side at heights between 20 m and 80 m (South region);
- the North side at the same heights (North region);
- the remaining parts of the chimney (other regions).

The North region and the other regions are presently in a better state compared to the South region, however they may be suffering ongoing deterioration and incipient damage, and so they may need to be repaired. The North region is inevitably linked to the South region, and the two will likely be subjected to the same method of intervention in spite of the different conditions of deterioration, whilst the remaining parts of the chimney can be considered independent. For each of the three zones, the thickness of concrete to be removed needs to be determined comparing the depth of carbonation and chloride penetration with the thickness of the concrete cover. To this aim, a detailed investigation campaign is necessary, that implies taking of concrete cores in sufficient number to evaluate the depth of carbonation and chloride penetration in the original concrete (investigations on the repair mortar are not necessary, since the mortar has to be removed in any case).

In the present case, at least 10 cores for each zone are necessary. The exact position of each core will be chosen with attention to the areas with higher risk, with a minimum distance of 2 m between adjacent cores. The cores shall be taken across the whole thickness of the concrete wall of the chimney. To limit the number of cores, and hence the costs and invasiveness of sampling, each core could be cut in longitudinal direction, so as to create two faces to perform colorimetric analysis aimed at determining the depth of carbonation (with an alcoholic solution of phenolphthalein) and the depth of chloride penetration (with a solution of fluorescein followed by a solution of silver nitrate) (Bertolini, 2008; Coppola & Buoso, 2015). No less than 2 cores for each region shall be tested in the laboratory to perform analyses for material characterisation (e.g., density, water absorption, compressive strength) and corrosion-related analyses (in particular, the quantitative determination of chloride profile).

Apart from sampling and destructive tests, an accurate visual observation will be necessary, combined with electrochemical measurements of mapping of reinforcement potential and concrete resistivity in representative regions, even in those areas that appear to be intact. These measurements are essentially non-destructive and hence they can be performed on wide areas. The measurement of the concrete cover thickness, which is totally non-invasive, shall be executed at least in the vicinity of the sampling areas, to allow a direct comparison with the results of colorimetric tests.

Based on the obtained results, once the thickness of the concrete to be removed is determined and before further evaluations on the intervention are made, structural assessment needs to be performed, aimed at checking the feasibility of the intervention and the need of strengthening during its execution. Given the risk of chloride contamination, great care needs to be dedicated to cleaning of the rebars from corrosion products. The rebars that will be exposed following concrete removal shall be checked to determine whether they need to be cleaned, even on the side facing backwards.

As far as the repair material is concerned (EN 1504, 2017), the use of a flowable mortar or self-compacting concrete (according to the thickness) is suggested. These materials can be poured inside moulds that, besides hydraulic tightness, provide protection from the environmental aggressiveness in the first hours or days after placing. Pouring in moulds allows to cast the whole thickness of repair material in a single layer, avoiding cold joints. Moreover, the repair material shall guarantee resistance to aggressive substances, hence it shall be a cementitious material with low w/c ratio and pozzolanic or hydraulic additions, besides superplasticiser admixtures. It shall be cured according to prescriptions from the producer, so as to avoid early damage (such as shrinkage cracking) and allow a correct hydration of cement, fully exploiting the beneficial effects related with the pozzolanic or hydraulic additions (such as fly ash and silica fume additions in various amounts). Given the high number of possible additions, the definition of the mix proportions is difficult to perform on-site. Premixed products are commonly used. On the market, a great variety of premixed mortar is available with various properties at the fresh and hardened state. Consequently, the designer should be able to express clear prescriptions on the required performances, so as to allow the choice of the most suitable product.

Apart from short-term properties of the repair material, such as workability at fresh state and mechanical properties, also long-term performances need to be considered to provide resistance to aggressive substances and protection to reinforcement for the expected service life. Given the great variety of repair products, the designer should be able to require clear prescriptions on the minimum performances, so as to allow the choice of suitable products. However, the parameters that describe the long-term behaviour of repair materials in a quantitative way (e.g. the resistance to carbonation or chloride penetration) are seldom reported on the technical data sheet. Nevertheless, in the scientific literature it is well known that a mortar with a low w/c ratio, containing pozzolanic or hydraulic additions, correctly placed and cured can provide a resistance to carbonation and chloride penetration that is comparable – if not higher – to that of a good quality concrete (Bertolini et al., 2006, 2013). Most repair products fulfil these compositional requirements and premature failure of the intervention is more likely due to execution-related aspects. Control tests on repair materials chosen for the intervention should be also planned in order to verify the fulfilment of the prescriptions of this specific application.

The repair material shall be applied in a way to guarantee an adequate cover thickness. This parameter shall be chosen by the designer based on both structural and durability requirements. From durability point of view, a design value of 50 mm could be chosen, in agreement with Eurocode 2 (EN 1992-1-1, 2004) that prescribes a minimum value of 45 mm for new structures exposed to the most severe exposure classes. Considering that the expected service life of the repair is 10 years, a design value of 50 mm can be considered more than adequate.

To prolong the service life of the intervention and to compensate for possible faults in execution due to reduced accessibility, reduced time and harsh microclimatic conditions, on the South region several methods of additional protection can be considered. More specifically, the resistance of the selected repair material to acid environment can be strengthened in two possible ways. A first strategy is based on the development of a repair material that is by itself suitable to guarantee an adequate resistance to acidic condensate thanks to a reduced permeability and porosity (in addition to the previously mentioned requirements for providing protection from corrosion).

However, such strategy would not be suitable if commercial premixed products will be used. The other strategy relies on the application of *surface treatments* that provide resistance to the acid environment. The selection can be made within a great variety of organic and inorganic products, able to provide a barrier effect and seal the pores thus preventing the ingress of aggressive agents (they are also referred to as film forming coatings). Given the mildly aggressive exposure to chemical attack and the required service life of the intervention, the use of surface treatments is likely the most cost-effective option, although they are subjected to deterioration and reduced effectiveness in time (Zivica & Bajza, 2001, 2002).

Moreover, the protection of reinforcement from corrosion can be prolonged – always on the South region – by the use of embedded galvanic anodes (Bertolini et al., 2013). Galvanic anodes are small elements of zinc embedded in a conductive material that exhibit a mechanism of cathodic protection to the steel reinforcement, hence reducing the corrosion rate on active rebars and inhibiting the effect of possible macrocells between rebars in different conditions of corrosion. The type, shape and number of anodes need to be determined in the framework of a dedicated design.

Lastly, considering the peculiar aspects of the chimney, its exposure conditions and history, it is suggested to implement a system for monitoring the corrosion conditions of the reinforcement, for example through embedded probes that allow the measurement of corrosion related parameters without the need of sampling or direct access to the chimney. Such system may allow to detect corrosion parameters in a continuous way, allowing to act promptly, before the deterioration phenomena are patent (also considering that the presence of a coating can mask the cracks). We suggest the use of reference electrodes for measuring the corrosion potential of the reinforcement (for instance, of the type silver/silver chloride, SSC (COST Action 521, 2003) that are available on the market), which can be fixed to the rebar prior to pouring the repair material.

Reference electrodes can be combined with probes for measuring the electrical resistivity of the cementitious material, which may allow to detect variations in its humidity content at the depth of the rebar and hence estimate the corrosion rate (Messina, Gastaldi, & Bertolini, 2017). Collected data need to be analysed and interpreted by experts. The use of sacrificial specimens can be considered, too, e.g. cubic specimens made of the same repair material and exposed to the same conditions of the South region (e.g., on the sidewalks). Such specimens will be easily accessible and retrievable for laboratory analyses to estimate the evolution of deterioration of the chimney.

Generally, for such reinforced concrete chimneys exposed to the action of similar aggressive conditions, only a regular inspection may allow detection of signs of degradation and, if necessary, application of remedial measures in an early stage of damage. Planning of inspection activities should be considered a priority in the design stage, on the basis of assumptions on the expected behaviour of the structure, required service life and of the aggressiveness of the exposure conditions.

5. Conclusions

Condition assessment of the reinforced-concrete chimney, located for 47 years in a working steel production plant in front of the Mediterranean Sea and repaired several times, has highlighted the level of environmental aggressiveness that, in particular, affected the South side of this structure for effect of the fumes coming from the nearby extinction tower. A synergic effect due to carbonation and chloride-induced corrosion of reinforcement and to the moderate chemical attack suffered by concrete due to exposure to fumes of the plant was identified. Moreover, based on the information coming from the investigation campaigns to which the chimney was subjected, the role of an incorrect design and execution of the repair interventions undergone can be evidenced; in particular with respect to the incomplete removal of non-protective concrete and unsuitable application of repair material.

In addition, it would be better to consider for a next repair intervention some formworks that allow the use of a repair material with flowable consistency in order to guarantee a perfect filling of the mould and embedding reinforcements, thus ensuring an adequate protection. Once placed, the repair material will have to be adequately cured. It is suggested to use a repair mortar with adequate additions or admixtures and a water/cement ratio low enough to guarantee resistance to carbonation and chloride penetration and strength. To prolong the service life of the intervention and to compensate for possible faults in execution due to reduced accessibility, reduced time and harsh microclimatic conditions, on the South region several methods of additional protection can be considered. More specifically, the application of surface treatments can improve the resistance to the aggressive environment. In addition, the protection of reinforcement from corrosion can be prolonged – always on the South region – by the use of embedded galvanic anodes.

Regarding the aggressiveness of the environment, it is assumed that no substantial changes will occur in the future. Hence, the next repair intervention will be required to guarantee the desired residual service life for the chimney in the same conditions of exposure. This can only be achieved if the intervention will be correct from a conceptual perspective (definition of the aims and principles in the design stage) as well as from an execution perspective (clear definition of a repair method and all the necessary steps). Lastly, considering the peculiar aspects of the chimney, its exposure conditions and history, it is suggested to implement a system for monitoring the corrosion conditions of the reinforcement.

Disclosure statement

No potential conflict of interest was reported by the authors.

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