Abstract. A lot of Reinforced Concrete (RC) structures in Syria have suffered from reinforcement corrosion which shortened significantly their service lives. Probably, one of the most effective approaches to make concrete structures more durable and concrete industry on the whole – more sustainable is to substitute pozzolan for a portion of Portland cement (PC). Syria is relatively rich in natural pozzolan. In the study, in order to predict the corrosion resistance from compressive strength, concrete specimens were produced with seven cement types: one plain Portland cement (control) and six natural pozzolan-based cements with replacement levels ranging from 10 to 35%. The development of the compressive strengths of concrete cube specimens with curing time has been investigated. Chloride penetrability has also been evaluated for all concrete mixes after three curing times of 7, 28 and 90 days. The effect on resistance of concrete against damage caused by corrosion of the embedded reinforcing steel has been investigated using an accelerated corrosion test by impressing a constant anodic potential for 7, 28 and 90 days curing. Test results have been statistically analysed and correlation equations relating compressive strength and corrosion performance have been developed. Significant correlations have been noted between the compressive strength and both rapid chloride penetrability and corrosion initiation times. So, this prediction could be reliable in concrete mix design when using natural pozzolan as cement replacement.

1. Introduction
Pozzolanic materials are being widely used as substitute for Portland cement because of their ecological, economical and performance-related advantageous properties [1-7]. Syria has important volcanic areas. More than 30,000 km² of the country is covered by Tertiary and Quaternary-age volcanic rocks [8], among which natural pozzolans constitute a considerable volume with the
estimated reserves of about three-quarters billion tonnes [9]. However, their potential use in making concrete is not well established. The cement produced in the country is almost of CEM I type, although an addition of natural pozzolan up to 5% was frequently used in most local cement plants. Hence, less than 300,000 tonnes of these pozzolans are only exploited annually (the annual production of PC in Syria is about 6 million tonnes) [10].

Compressive strength of concrete is commonly considered its most valuable property, although in many practical cases other characteristics, such as durability and permeability, may in fact be more important [11]. Therefore, designers should not ignore the environmental conditions taking into consideration only the strength as the sole criterion in their structural designs [12].

Chloride-induced corrosion is currently considered to be the most important and most serious deterioration mechanism for RC structures [13-14]. Corrosion of reinforcing steel is an important problem faced by the construction sector in Syria, especially in industrial and marine environments. A lot of RC structures have suffered from this phenomenon, which shortened significantly their service lives.

In order to make the concrete industry much more sustainable, it is imperative to employ some effective approaches in concrete mix design. Probably one of the most effective approaches is to substitute pozzolan for a portion of PC; each 1kg of substitution reduces the emission of CO$_2$ by about 1 kg, and saves the energy required to produce 1 kg of cement. In addition, these pozzolans could be used to make stronger and more durable concretes [12].

Compressive strength measurements are easy from an experimental point of view. By contrast, evaluation of reinforcement corrosion resistance is time consuming and difficult to deal with. In the study, in order to predict corrosion resistance from concrete compressive strength, compressive strength, rapid chloride penetrability and corrosion initiation times were experimentally investigated. Furthermore, relationships among some investigated properties were analysed in this paper. The study is of particular importance not only for the country in question but also for other countries with similar geology, e.g. Harrat Al-Shaam, a volcanic field covering a total area of some 45,000 km$^2$, a third of which is located in Syria. The rest covers parts of Jordan and Saudi Arabia.

2. Materials and methods

The natural pozzolan used in the experiments was quarried from Dirat-at-Tulul site, about 70 km southeast of Damascus as shown in figure 1. The mineralogical analysis showed the pozzolan is mainly composed of amorphous glassy ground mass, vesicles, plagioclase and olivine with the following percentages – 20%, 35%, 20% and 25%, respectively (based on the optical estimate). Thin sections of the investigated pozzolan are shown in figure 2. The chemical analysis of pozzolan used in the study is summarized in table 1.

Seven cement samples were prepared in accordance with EN 197-1; one plain PC CEM I (control), three CEM II/A-P samples with three replacement levels of pozzolan (10, 15 and 20%), and three CEM II/B-P samples with three replacement levels (25, 30, 35%), respectively. 5% of gypsum was added to all these cement samples. The clinker was obtained from Adra Cement Plant, Damascus, Syria. Chemical analysis of clinker and gypsum is shown in table 1. All samples were interground by a laboratory grinding mill to a Blaine fineness of 3200±50 cm$^2$/g. CEM I (the control sample) was designated as CEM I, whereas pozzolan-based cements were designated according to the replacement level. For instance, CEM II/10% and CEM II/35% refer to the cements containing 10% and 35% of pozzolan, respectively.
Seven concrete mixes were prepared using grading of aggregate mixtures kept constant for all concretes. Aggregates used in the study were crushed dolomite with natural sand added. Chemical composition of the aggregates is illustrated in table 1. Their quantities in 1 m$^3$ concrete mix based on the oven-dry condition are as follows: 565.5 kg of coarse aggregate, 565.5 kg of medium-size aggregate, 447.5 kg of crushed stone sand and 286.5 kg of natural sand. All concrete mixes were designed to have a water-binder ratio (w/b) of 0.6 and a slump of 150±20 mm. No chemical admixture was added. Concrete cubes (150 mm) and concrete cylinders (100 mm×200 mm) were cast for the determination of compressive strength and evaluation of the penetrability of chloride ions, respectively. The reinforced concrete specimen for the accelerated corrosion tests was 100×200 mm concrete cylinder in which 12 mm diameter steel bar was centrally embedded. The steel bar was embedded into the concrete cylinder so that its end was at least 45 mm from the bottom of the cylinder, and it was coated with epoxy at the exit from the concrete cylinder in order to eliminate crevice corrosion at these locations.

![Figure 1. Map of Harrat Al-Shaam and the studied site.](image-url)
Figure 2. Thin sections of N pozzolan. a) Microphenocrysts of Olivine in volcanic glass matrix with vesicles, some of which are filled with white minerals; b) Microphenocrysts of elongated plagioclase in volcanic glass matrix with vesicles, some of which are filled with white minerals.

The compressive strength development was determined on 150 mm cubic concrete specimens, in accordance with ISO 4012, 1978, at ages of 7, 28 and 90 days.

The rapid chloride penetrability test was conducted in accordance with ASTM C 1202. Three cylinder specimens of each concrete mix were tested after 7, 28 and 90 days curing.

An accelerated corrosion test was used to compare the corrosion performance of concretes containing cements produced. Similar techniques with little differences were reported by other researchers [15-23]. In the study, RC specimens were immersed in a 15% NaCl solution leveling the half of the concrete cylinder and the steel bar (working electrode) was connected to the positive terminal of a DC power source while the negative terminal was connected to a steel plate (counter electrode) placed near the concrete specimen in the solution. The corrosion process was initiated by impressing a relatively high anodic potential of 12 V to accelerate the corrosion process. Figure 3 shows a schematic representation of the experimental setup for the accelerated corrosion test. The specimen was monitored periodically to see how long it takes for corrosion cracks to appear on the specimen surface. The current readings with time were recorded at 3-4 hours-intervals. Three specimens from each concrete mix were tested after 7, 28 and 90 days curing.
3. Results and discussion

3.1. Compressive strength of concretes

Results of compressive strength test are plotted in figure 4. As expected, the compressive strength of the concrete increased with curing time with a high rate of strength gains at early ages which gradually decreased at longer ages. Plain cement concrete specimens have higher compressive strengths at any age when compared to pozzolan-based cement concretes. This diminution of strength of pozzolan-based cement concretes was higher at early age and increased with the percentage of pozzolan. The compressive strength at 7 days decreased from 24.9 to 16.0 MPa when CEM I and CEM II/35% of pozzolan were used, respectively. This could be explained by the slowness of the pozzolanic reaction between the glassy phase in pozzolan and the calcium hydroxide released during cement hydration [24]. However, due to the continuation of this reaction and the formation of a secondary CSH, a greater degree of hydration was achieved resulting in strengths after 90 days curing, which were comparable to those of CEM I specimens.

3.2. Rapid chloride penetrability

From the rapid chloride penetrability data, figure 5, it should be noted that the CEM I-based concrete permitted almost 2 or 3 times the coulombs charge, when compared to the concrete containing CEM II/B in spite of the fact that all concretes were made with similar cementitious content and water
content. None of concretes has the total charge passed less than 2,000 coulombs after 7 or 28 days curing. This expected result may be due to the high w/b ratio. However, the concretes containing CEM II/B-P showed the best performance among all specimens. According to ASTM C1202, these concretes can be considered as low chloride permeable after 90 days curing.

![Figure 4. Cubic compressive strength of concrete specimens based on curing age.](image)

The improvement in resistance to chloride penetration may be related to the refined pore structure of these concretes and their reduced electrical conductivity [25]. This, as it was confirmed by many researches [26-28], is due to the secondary pozzolanic reaction which contributes to making the microstructure of concrete denser.

![Figure 5. Rapid chloride penetrability of concrete specimens based on curing age.](image)

3.3. Corrosion resistance
The accelerated corrosion behaviour of steel bars embedded in concrete specimens was studied by impressing a constant anodic potential. The current required to maintain the fixed potential was plotted against time and typical curves of corrosion current versus time for the concrete specimens are illustrated in figure 6. As seen from figures 6, current–time curve initially descended till the time period, after which a steady low rate of increase in current was observed, and after a specific time period a rapid increase in current was detected until failure. Almost a similar variation of the corrosion current with time has been also observed by other researchers [15, 19]. The first visual evidence of corrosion was the appearance of brown stains on the surface of the specimens. Cracking was observed shortly thereafter, and it was associated with a sudden rise in the current. Figure 7 presents the average...
corrosion initiation times required to crack the specimens made with CEM I, CEM II/A-P and CEM II/B-P. Time to initiate corrosion in CEM I concrete specimens was in the range of 52-106 h (2-4.5 days), whereas that in CEM II/B-P was in the range of 83-370 h (3.5-15.5 days), depending on the replacement level and the age at testing. The times of corrosion initiation for the pozzolan-based cement concrete specimens were longer than the plain cement concrete specimens, which indicated that the former provided better protection to steel reinforcement against corrosion. This delay in corrosion time when using blended cements, particularly at longer ages of curing, may be related to the pozzolanic reaction, which contributes to filling the voids and pores in the concrete with an additional CSH gel. This leads to decrease of pore size and to a smaller effective diffusivity for chloride. This can improve the long-term corrosion resistance of reinforced concrete structures and make concrete denser and less permeable [19, 29].

Figure 6. Typical curve of corrosion current versus time of concrete specimens tested after 90 days curing.

![Figure 6](image)

Figure 7. Corrosion initiation times of reinforced concrete specimens based on curing age.

3.4. Corrosion initiation time versus chloride penetrability
It was observed from figure 8 that the corrosion initiation time and chloride penetrability of concrete are closely related. The analysis results showed that there was an excellent correlation between corrosion initiation time and total charge passed through pozzolan-based cement concrete specimens, with a regression coefficient ($R^2=0.95$). According to Montgomery [30], a regression coefficient, $R^2$, of more than 0.85 indicates an excellent correlation between the fitted parameters. Increasing the total charge passed through concrete specimens reduces the time to initiate corrosion.
3.5. Correlation between compressive strength and durability-related properties

The rapid chloride penetrability and corrosion initiation times were plotted against the compressive strength in order to develop the relationship between these properties in pozzolan-based cement concretes (CEM II/P). These relationships are illustrated in figures 9-10. The relationships between compressive strength and chloride penetrability for each curing time are illustrated in figure 9. The high correlation coefficients of not less than 0.86 for all curing times indicated that there were significant linear correlations between compressive strength and RCP.

![Figure 8. Variation of corrosion initiation time with rapid chloride penetrability.](image)

Based on figure 10, there were good linear correlations between cubic compressive strength and corrosion initiation time for each curing time. It can be seen that after 90 days curing, the corrosion initiation time showed a higher rate of increment indicated by the steep slope of the curve, when compared to both 7 and 28 days curing. It can also be seen that the relationships between compressive strength and each of RPC and CIT are greatly affected by curing time. Contrary to expectations, the increase in strength did not increase the corrosion resistance, as clearly seen in figures 9 and 10. According to the authors, this could be explained as follows: a) firstly, this was in agreement with Neville [11] who indicated that the assumption that 'strong concrete is durable concrete' is not always true, b) secondly, as indicated in the paper, the lower early compressive strength of the blended cement could be attributed to the slow pozzolanic reaction [24], c) thirdly, the low permeability of the blended cement at early ages could mainly be attributed to the filling effect of pozzolan, which can be more finely grained than clinker when they are ground together [31].

The general correlation formulas between each chloride penetrability & corrosion initiation time and compressive strength can be expressed as follows, with regression coefficients ($R^2$) in brackets:

\[
\text{RCP} = (-6.83t + 846)f_{cu} + 3.74t^2 - 366t - 4043 \quad (R^2=0.96) \quad (1)
\]

\[
\text{CIT} = (-0.26t - 4)f_{cu} + 12.62t + 101 \quad (R^2=0.97) \quad (2)
\]

where RCP is the rapid chloride penetrability of concrete (in coulombs), CIT is the corrosion initiation time (in hours), $f_{cu}$ is cubic compressive strength of concrete and $t$ is curing age. Correlations between the measured values and the values calculated according to these equations for each of RCP and CIT are illustrated in figure 11 and figure 12, respectively.
4. Conclusion

From the experimental results, the following conclusions could be drawn:

- The cubic compressive strengths of concrete containing pozzolan-based cements were much lower than that of plain cement concrete at all early ages of concrete. However, at 90 days curing, the compressive strengths of pozzolan-based concretes were comparable to those of plain cement concrete.

- The chloride penetrability of pozzolan-based concrete mixes is much lower than that of plain concrete, especially at high replacement levels of pozzolan.

- According to the results of the accelerated corrosion test, concretes produced with pozzolan-based cements decelerated rebar corrosion. Particularly, CEM II/B-P cement types with 25, 30 and 35\% pozzolan content were found to delay corrosion significantly. Use of pozzolan at 30\% cement replacement level makes the service life of the RC structure under chloride-bearing environments longer twice or thrice when compared to the control.

- A definite correlation is observed between the rapid chloride penetrability test and the accelerated corrosion test, so that one can be estimated from the knowledge of the other.
Curing has a large influence on both compressive strength and durability properties of pozzolan-based cement concrete. However, the consequences of short-term curing can be more serious for the latter.

The development of good relationships between compressive strength and corrosion resistance properties of pozzolan-based cement concrete can be of considerable benefit. Compressive strength, which is easier to measure, can be reliability applied to predict some performance-related properties of concretes containing similar pozzolans, including rapid chloride penetrability and corrosion initiation time. However, this prediction can’t be used for all pozzolan-based cement concretes.

Based on the test results, it is suggested that pozzolan can be used up to 30% as a partial substitute for PC in production of blended cements. This addition ratio can reduce the quantity of CO$_2$ released by Syrian cement plants by about 1.5 million tonnes and the consumed energy by about 30% annually. So, production of green concrete could be promoted.

5. References

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