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ORIGINAL PAPER

Opuntia-Ficus-Indica (Nopal) mucilage as a steel corrosion inhibitor in alkaline media

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Abstract This paper presents results on the corrosion performance of reinforcing steel in alkaline media when dehydrated Opuntia Ficus Indica (Nopal) was used as an admixture. The dehydrated Nopal material was mixed with saturated calcium hydroxide (SCH) at 0.5, 1.0, and 2.0% by weight. Half cell potentials and Linear Polarization Resistance (LPR) measurements were performed at different time periods to characterize the corrosion inhibiting effect of the admixture. Results showed good corrosion inhibiting effect of dehydrated Nopal on reinforcing steel. The polarization resistance (R_P) value increased from an average of 40 kΩ cm^2 for regular chloride-contaminated SCH solution, to an average of 150 kΩ cm^2 for Nopal-added chloride-contaminated SCH solutions. The addition of Nopal led to the formation of a denser and more packed oxide/hydroxide surface layer on the steel surface that decreased corrosion activity. This oxide/hydroxide layer growth was confirmed from microscopic evaluation of the metal surface layer performed at the end of the experiment.

Keywords Alkaline media · Corrosion inhibitor · Natural organic additions · Nopal · Opuntia Ficus Indica · Polarization resistance · Reinforcing steel

1 Introduction

Corrosion inhibitors are widely used in concrete, where conventional formulations often include species (such as nitrite or benzoate) that have significant toxicity. As a result, these are being scrutinized by environmentalists.

Ashassi-Sorkhabi et al. [1] considered the use of the simple amino acids alanine, glycine and leucine as corrosion inhibitors for carbon steel in hydrochloric acid. Natural amino acids are also being tested as inhibitors [1–6]. The extracts from cactus plants are the most promising [4, 6]. A common type of cactus plant used for this purpose is known as Indian fig or Opuntia ficus-indica (OFI). Originally a native of Mexico, it is now cultivated in Mediterranean regions of Europe, South and Western United States, and throughout Latin America. Today the cactus is commercially grown in Mexico, Chile, Argentina, Morocco, Italy, and parts of California, Texas, and Florida [7]. The ancient Aztecs also used it for medicinal purposes as described in the Aztec Herbal of 1552 [8–9]. They referred to it as ‘‘Nohpalli.’’ Today in Mexico it is commonly referred to as ‘‘Nopal.’’

Several species of Nopal cactus have been employed as sources of traditional additives in the production of lime plasters and the conservation of earthen Architecture in Latin America [8–10]. For example, one of the currently widespread conservation practices is to use the water residue from boiling of the commonly available Nopal cactus in the production of lime putty, which is then used as a finishing coat on lime plaster to protect or repair adobe churches and/or Missions in Mexico and the American Southwest [8–9].

The chemical and industrial analyses of the Nopal cactus liquid, commonly called ‘‘Mucilage,’’ indicate that it contains a large amount of pectin and various sugars [11].

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The mucilage from the pads is similar to that of Aloe Vera: it is thick and slimy. Several mechanisms for the observed improvements resulting from the addition of Nopal mucilage have been suggested in the conservation and building materials literature [8–10].

Torres-Acosta et al. studied the effect of dehydrated Nopal or Aloe Vera powder additions on the electrochemical performance of reinforcing steel in chloride contaminated concrete [12]. The preliminary findings suggest that adding these powders in small concentrations might be suitable for enhancing corrosion resistance of steel in concrete [12]. But the role of how such additions in enhancing corrosion performance is not as yet well understood. One possibility is that the mucilage acts as a pore clog, stopping the penetration of chlorides and/or water through the concrete pore network by forming a chemical bound between the pectines and chloride/water molecules [11]. The other could be that mucilage acts as a corrosion inhibitor for steel in chloride-contaminated concrete, similar to what was observed in a previous study where Nopal mucilage acted as a corrosion inhibitor of aluminum and steel in acidic solutions [4, 6].

Therefore, this investigation deals with the performance of Nopal mucilage as a corrosion inhibitor of steel in concrete-like environment (alkaline solutions) when chloride contamination is present. An alkaline solution was chosen to study the effect of one variable only, and leaving behind the possible effect of pore clog in mortar or concrete.

2 Experimental procedure

2.1 Steel

The steel samples used in the tests were deformed reinforcing steel bars (rebars) 9.5 mm nominal diameter. The rebar surface was in the as-received condition, with the original mill scale in place, but cleaned with acetone before casting.

2.2 Electrochemical cell

Four electrochemical cells were used: the first served as a control cell with only saturated calcium hydroxide (SCH) solution with a typical pH of 12.5, and the other three with a similar SCH solution plus 0.5, 1.0, and 2% by weight of Nopal (% by weight of solution). Six rebar specimens were placed inside each cell. The nominal surface area of the steel specimens in contact with the electrolyte was ~30 cm^2 each. Figure 1 shows a schematic of the cell configuration. An epoxy coating was placed at the upper end of the rebar to avoid corrosion due to aerating differences on the rebars. Individual electrical connections of each rebar specimens were made to external wiring using a stainless steel screw.

The experiments (all at 22 ± 2 °C) involved two consecutive stages:

a. Stabilization stage, in which the specimens were placed inside each cell until potential stabilization of the steel rebar was achieved (0 till 24 days).
b. Chloride contamination stage (25 till 128 days), where each electrochemical cell was contaminated in four steps, approximately once every week, by adding either 0.04 or 0.08 M NaCl (0.7 or 1.4 g) at each step.

2.3 Electrochemical measurements

Potential measurements of the steel rebar specimens were periodically made using a 200 MΩ impedance DC voltmeter. They were measured versus a Saturated Calomel Electrode (SCE) placed inside each cell every time the potential was measured.

A PCI4/750 Corrosion Measurement System from Gamry Instruments, Inc., was used to measure the apparent polarization resistance (R_P) values of the rebar during all stages. The selected rebar sample was connected as a working electrode to a potentiostat. The reference electrode was the SCE, and the counter electrode was a stainless steel plate. The impressed potential was varied from the open circuit potential (OPC) in the cathodic direction, by an amount of 20 mV with a scan rate of 0.05 mV s^{-1}. The R_P value of the rebar was estimated from the slope of the final portion of the potential-current data, which normally was a straight line the last 10 mV of the scan.

2.4 Microscopic analysis

A microscope analysis of the steel rebar at the end of the experimental period was also performed. After the exposure period, steel rebars were taken out of the SCH solution and allowed to dry for 7 days in a laboratory environment (20 ± 2 °C, 65 ± 5% RH). The rebar surfaces were then photographed using an Optical Microscope. Between six to eight segments of the rebar surface were photographed. The micrographs of the segments were then reviewed and comparisons made.

3 Results and discussion

3.1 Half cell potentials

Figure 2 shows the half cell potentials as a function of time for typical measurements obtained from (a) no addition (control SCH solution), (b) 0.5% Nopal, (c) 1% Nopal, and

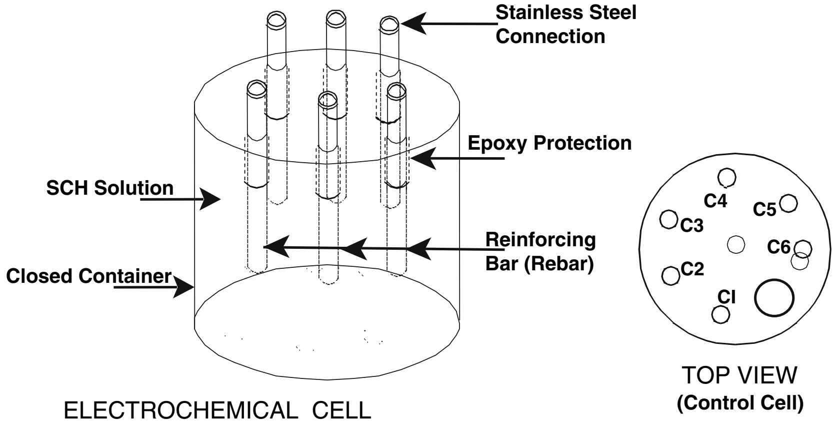


Fig. 1 Electrochemical cell configuration (Control cell)

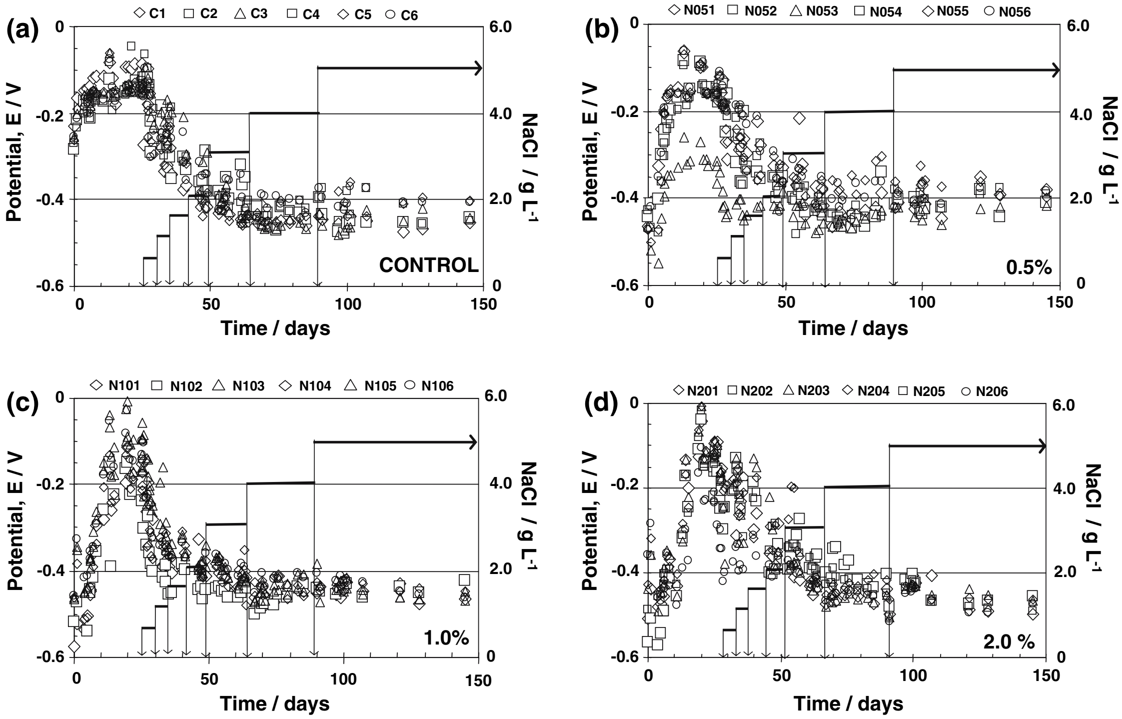


Fig. 2 Potential vs. Time. (**a**) Control, (**b**) 0.5%, (**c**) 1%, and (**d**) 2%. The horizontal lines correspond to the NaCl contamination steps

(d) 2% Nopal cells, respectively. Initially, during the stabilization stage, potentials for rebars in SCH (controls) solution reached higher values (~–0.10 mV vs. SCE), as compared to all other cells with SCH + Nopal, where potentials gradually increased from values as low as –0.55 V (vs. SCE) until values similar to the controls were attained after 20 days. This gradual change from high negative potentials (which in turns means active corrosion) to less negative potentials might be due to oxygen depletion on the electrolyte, which in turn decreases the oxide/hydroxide formation rate on the rebar surface in the Nopal-added SCH solution [13]. The oxide layer (or layers) formed on the rebar surface then apparently passivates and the rebar corrosion activity slows down in such electrolyte with Nopal. This performance will be discussed with the R_P results following.

Figure 2 also includes half-cell potential results when chlorides were added to each of the electrochemical cells starting from day 25. The arrows in Fig. 2 indicate the actual days where the chlorides were added to the solution. Similar potential behavior was observed between control and Nopal-added cells when chlorides were introduced: the potential dropped dramatically, from the passive stage (–0.10 V vs. SCE) to more active potentials (–0.45 V vs. SCE). Small differences were observed between the rebar half-cell potential values in SCH solution and those obtained from rebars in Nopal-added SCH solutions. The rebar potentials for Nopal-added solutions were a few millivolts more positive than those from the Nopal-free solution (control rebars).

3.2 Linear polarization resistance

The R_P value has been used for some time as a indirect measure of corrosion rate of steel in concrete (and other electrolytes) by using a well known relationship: $i_{CORR} \sim B \times 10^6 R_P^{-1}$, where i_{CORR} is the apparent corrosion rate (in μA cm^{-2}), B is a constant obtained with the Tafel slopes (in V) and equal to ~0.026 V for active steel, and ~0.052 for passive steel [14].

Figure 3 shows the average R_P data (average from six rebars) as a function of time for all the electrolytes tested. The data for the control rebar (without Nopal) during stabilization delineates behavior typically observed in polarization tests of steel reinforcement in uncontaminated alkaline media [14] with values up to 1,000 kΩ cm^2. But the values registered with Nopal-added solutions during the same stage were initially low (between 100 and 200 kΩ cm^2), reaching similar values to the controls at the end of the stabilization stage (~1,000 kΩ cm^2). This behavior supports what was observed from the potential measurements. There may be two explanations for this phenomenon: the formation of a more dense oxide film at the rebar interface or the fact that Nopal acts as an oxygen scavenger. The apparent increase in the corrosion rate of the rebar during the stabilization stage, generating more corrosion products (oxides or hydroxides) on the metal surface supports the first hypothesis. After some time the oxides create a barrier against further corrosion of the rebar, as observed from the average R_P data measured and shown in Fig. 3.

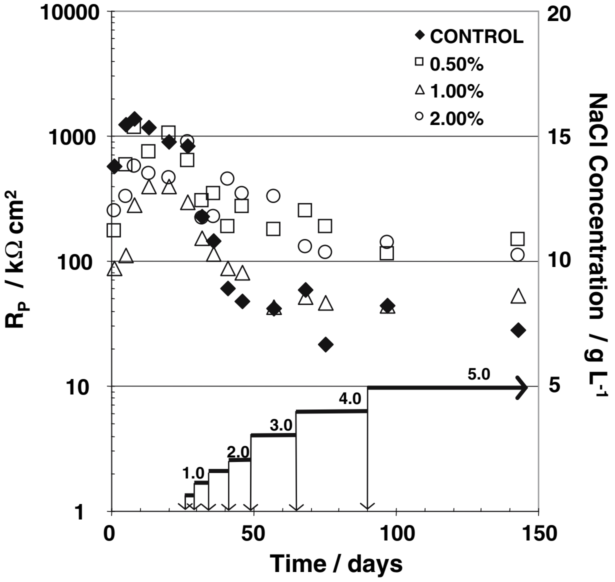


Fig. 3 Average R_P vs. Time for all electrochemical cells tested. The horizontal lines correspond to the NaCl contamination added (in g L^{-1})

As observed in Fig. 3, the R_P values for the control cell during the chloride contamination stage (after day 25) decreased to a value near 40 kΩ m^2 (on average) at the end of the chloride contamination stage. The same behavior was observed with the rebars for Nopal-added cells, but the R_P change rate was smaller than the control rebars in the SCH cells. At the end of the chloride contamination stage the R_P values were on average 150 kΩ m^2. This gives an initial trend where higher R_P values (smaller apparent corrosion rates) of steel in chloride contaminated SCH solutions were obtained when Nopal was added to the electrolyte.

To demonstrate this trend, Fig. 4 shows the R_P value distribution for all the rebars tested in the four electrochemical cells studied and at four different exposure times. These values are represented in a cumulative probability distribution format, where the R_P results were ordered from lower to higher value and plotted as the ''x-axis.'' The ''y-axis'' was the cumulative probability.

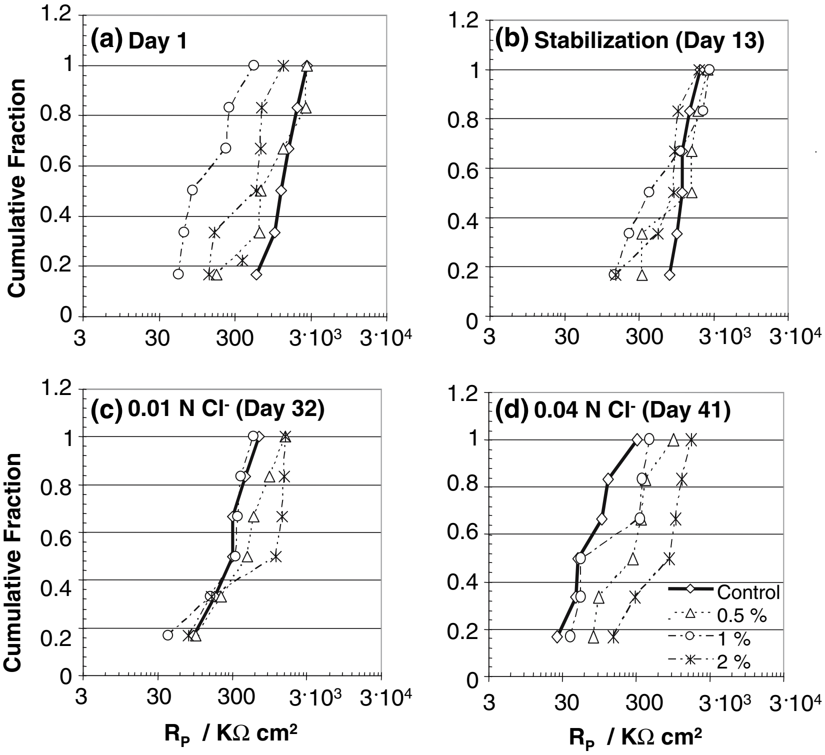
R_P results in Fig. 4a for values obtained just after the rebars were placed inside the free-chloride SCH solutions, show S-shaped distributions, shifting to the left (lower R_P values) those obtained from Nopal-added solutions. As time continued up to the end of the stabilization stage (day 25) the R_P distributions tended to be quite narrow and all rebar specimens showed similar R_P values regardless of Nopal content (Fig. 4b). When the chlorides were added (Figs. 4c,d), the R_P distributions for the control specimens shifted to the left as the chloride content was increased, in contrast to what developed for the rebar specimens in the Nopal-added cells, which stayed almost unchanged despite the chloride addition. This behavior supports the theory that Nopal inhibits corrosion of the rebar when chloride contamination puts in jeopardy the corrosion resistance of the metal in an alkaline environment.

Inhibition efficiency (IE in %) estimates were calculated from Eq. 1 [15]:

$$\mathrm{IE}\% = \frac{R_{t0}^{-1} - R_{ti}^{-1}}{R_{t0}^{-1}} \times 100 \qquad (1)$$

where R_{ti} and R_{t0} are the apparent polarization resistances with and without Nopal additions, respectively, at time t. Figure 5 presents the results of IE% as a function of chloride concentration in the alkaline solution. The IE% values for almost all Nopal-added solutions were higher than 70%. Only the 1% Nopal solution showed a marginal improvement (IE% ~ 50%) due to the formation of corrosion underneath the epoxy at the rebar ends. The rest showed more reliable performance at IE% ~ 85% and remained constant for chloride concentrations higher than 1.5% (see Fig. 5).

Fig. 4 Single R_P Measurements at different time stages ordered and represented as cumulative probability distributions. ◇ = Control, Δ = 0.5%, ○ = 1%, × = 2%



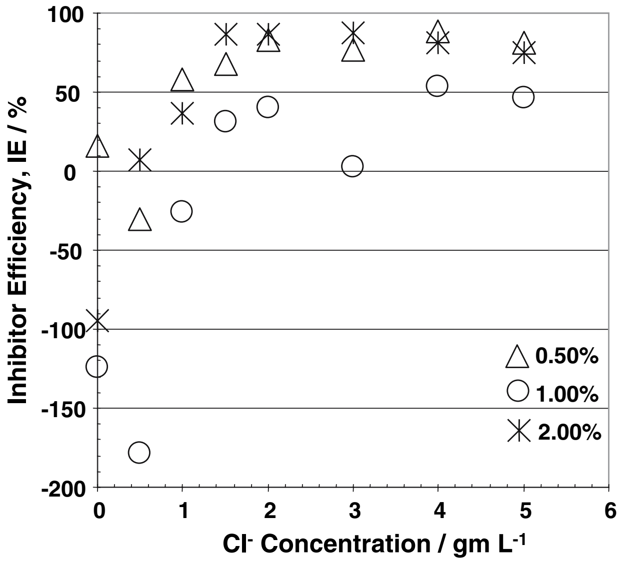


Fig. 5 Inhibitor efficiency (IE%) vs. chloride concentration in the electrolyte

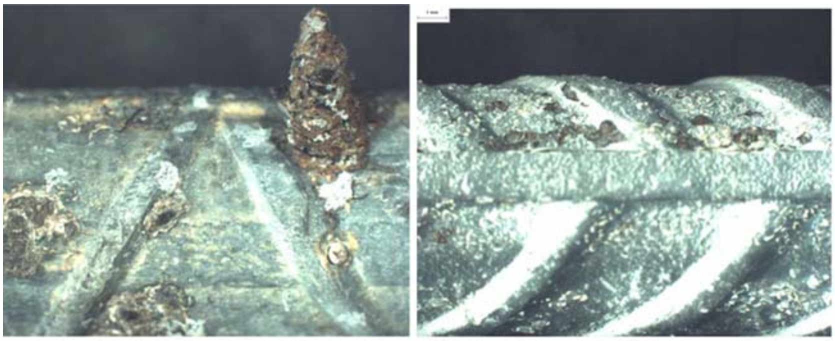
The inhibiting performance of Nopal presented in this investigation seeks to simulate a chloride contaminated concrete environment. But more experimental information is needed to extrapolate the results obtained for concrete structures, due to the fact that concrete pores are not always saturated with water. Several mortar and concrete specimens were fabricated in the past two years and experimental data will be available to support these findings in the near future.

3.3 Microscopic analysis

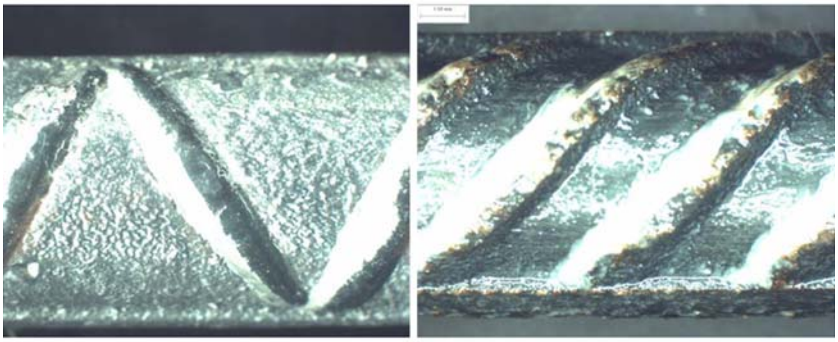
To support these theories microscopy was performed on all rebars from each SCH solution. Figure 6 shows four photographs taken from rebars from each test electrolyte. Showing active pitting areas. All the rebars in the control solution presented pits (corrosion products accumulation areas) as compared with those in Nopal-added solutions, where no pits were present in some cases.

The number of pits was recorded and Fig. 7 shows those numbers as a cumulative distribution, similar to R_P results presented in Fig. 4. From Fig. 7 Nopal addition is seen to inhibit the formation of active areas or pits, supporting the inhibiting action of this addition over reinforcing steel in chloride-contaminated alkaline media. All rebars in Nopal-added solutions had fewer pits (between 0 and 7 pits) compared to those in the control solution without Nopal addition (between 8 and 18 pits). Nopal concentrations higher than 1% enhanced the corrosion resistance of steel, as observed from the number of pits formed, which were between 0 and 4, as compared with 0.5% Nopal with the number of pits between 1 and 7. Nevertheless, the average number of pits for all Nopal

Fig. 6 Microscopic photographs obtained from typical rebar immersed in each electrolyte tested



Control – C1 **0.5% - N053**



1% - N106 **2% - N202**

solutions differed only by one pit. For the 1 and 2% Nopal concentrations this difference was two (1%) and three pits for 0.5% Nopal concentration.

The results presented here in combination with kinetic results in mortar and concrete specimens based on Electrochemical Impedance Spectroscopy (for interface change characterization) and Cyclic Polarization (for possible oxygen depletion in the electrolyte when Nopal is added) are currently being examined and results will be presented in the future.

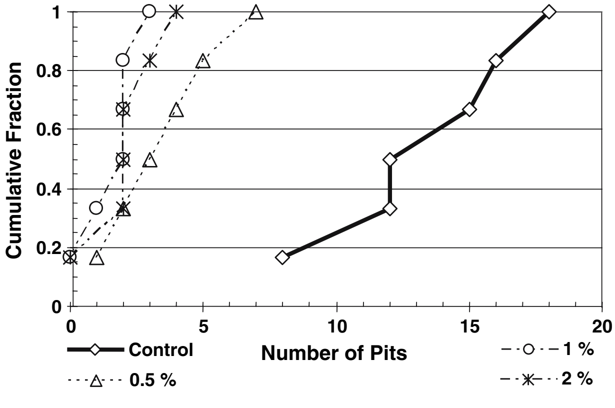


Fig. 7 Number of pits observed on the rebar from each of the solutions tested

4 Conclusions

Laboratory tests were conducted to investigate if a cactus addition, Nopal (Opuntia Ficus Indica), behaved as a corrosion inhibitor of reinforcing steel in chloride contaminated alkaline solutions. The results indicate that the dehydrated Nopal tested is a potentially useful addition to enhance the corrosion resistance of reinforcing steel when added to saturated calcium hydroxide solutions in percentages less than 2%. Polarization resistance tests values of reinforcing steel in such alkaline solutions with Nopal additions were about four times higher than values for the same steel in alkaline solutions without such additions (without Nopal ~40 kΩ cm^2 vs. with Nopal ~150 kΩ cm^2 in average). Based on a microscopic surface survey performed after testing, the corrosion resistance improvement was apparently due to a denser oxide/hydroxide film formation on the reinforcing steel when Nopal reacted chemically with the metal which, in turn, inhibited pit formation when chlorides were added to the electrolyte.

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