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EFFECT OF BIOFOULING ON CATHODICALLY PROTECTED CARBON STEEL IN SHALLOW SEAWATERS EXPOSED TO SUNLIGHT PHOTOPERIOD

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ABSTRACT

Here presented research deals with carbon steel samples cathodically protected with Zinc anodes controlling applied potential with resistances in the window for oxygen limiting discharge (-850±50 mV Ag/AgCl). Characterization of biofouling effects was made through comparison between electrodes immersed in aged tank of natural seawater and a control tank filled with not biologically active seawater. Both tanks were exposed to sunlight photoperiod for several days during the summer 2008. Cathodic current behaviours were monitored during dark hours, sunlight hours and during sunlight interruptions via temporary tank coverage. Observed variations showed that the biolayer induces appreciable and diversified effects. Particularly, these are considered to be induced by active contribution (O_2 production/consumption cycles) and passive contribution (O_2 diffusion shielding from the bulk), in addition to the passive one performed by underlying calcareous deposit *per se* growing under cathodic polarization in seawaters.

INTRODUCTION

Cathodic protection of metals in sea waters results from the combination of intrinsic parameters related to the structure to be protected (metal, applied potential, time of polarization) and surrounding parameters characterising the medium in which the protection occurs (T, pH, hydrodynamic regime, O_2 concentration, *etc.*~~.~~). Many studies have been carried out in the last decades in order to evaluate cathodic protection performances in different seawater environments and conditions. Hydrodynamic regime [Lee, 1986; Mentel, 1992], temperature [Barchiche, 2004; Dexter, 1986] and pressure [Chen, 2002; Chen, 2003] were investigated. Nevertheless, at the best of our knowledge, a lack exists about CP in shallow photic seawaters. The interest of CP in this compartment should arise from a characterization *per se* and the verification of its real contribution to the whole CP balance.

It is known that a beneficial effect to the CP performance in seawater is provided by the formation of the calcareous deposit. This mineral layer growing at the metal-solution interface once a cathodic potential is imposed makes more difficult the oxygen flux towards the underling metal. This reduces the currents required to maintain the polarization potential. In seawaters, the formation of a mineral layer on a cathodically protected metals results from the shift HCO_3^-/CO_3^{2-} equilibrium towards the production of CO_3^{2-} [Barchice, 2003] as a consequence of the alkalinity produced at the cathode through the following reactions:

1) $O_2+2H_2O\rightarrow 2OH^-+H_2$;

2) $HCO_3^- + OH^- \rightarrow CO_3^{2-}$.
3) $CO_3^{2-} + Ca \rightarrow CaCO_3$.

At potentials inducing the oxygen limiting discharge (-850±50) mV Ag/AgCl the $CaCO_3$ precipitation occurs, while at more cathodic potentials $Mg(OH)_2$ starts to precipitate [Barchice, 2003].

About CP performance in seawater, it would be interesting to verify how CP behaves in the photic zone, where all the physical-chemical parameters affecting CP undergo daily and seasonal oscillation induced by the natural photoperiod.

Experiments concerning control conditions were performed in a 3 days period exposing cathodically protected carbon steel electrodes to summer sunlight cycles in absence of biological components [Benedetti, 2009]. These tests showed that at –850 mV Ag/AgCl and in absence of a growing calcareous deposit, i_LO_2 (oxygen limiting currents) enhanced during daylight hours and that the main cause was the solar radiation rather than the induced heating of the solution bulk. In presence of $CaCO_3$ daily current enhancements were reduced but not eliminated, still remaining the solar radiation the main cause of currents rise.

Once immersed in natural seawater, a metal surface under cathodic protection undergoes calcareous deposit growth and biologic colonization.

The first was largely studied as previously mentioned, the second is rather complex [Alem, 1957; Cooksey, 1995], and their combination is still not well characterized in general.

Here presented results regard the investigation of the potential range inducing O_2 limiting discharge in photic seawaters since oxygen is 1) the main cathodic reactant and 2) a key molecule in the examined environment. About natural photic seawaters, we considered interesting to characterize the combination of factors modifying the O_2 balance at the electrode-solution interface (i.e. CP performance), particularly the mere passive effects performed by the calcareous deposit and passive-active effects performed by the biofouling under the natural photoperiod.

The research presented here had two aims: (1) to verify whether sunlight effects last beyond 72 hours in presence of calcareous deposit only (absence of biology), and (2) to give a first simpler approach on the investigation about calcareous deposit and biofouling combined effects under the photoperiod. So, it was decided to cathodically protect carbon steel electrodes in biologically inactivated seawater (sunlight effects in presence of the calcareous deposit only) and successively to move half of the cathodes in the biological tank (evaluation of biological effects). Both phases were performed and monitored under the natural photoperiod.

The investigated potential range was always -850±50 mV vs. Ag/AgCl (O_2 limiting currents).

2. MATERIALS AND METHODS

2.1 Experimental environments.

Polarizations were performed at the MARECO marine research laboratory of the IENI-CNR Institute, located in Bonassola, on the Ligurian Coast of the Mediterranean Sea. The tests were conducted during Summer 2008.

The experiments were made in two 200L tanks placed on the laboratory's roof and exposed to the natural photoperiod. The first tank (named "B") was filled with natural seawater. The second tank (named "BI", control) was filled with not filtered natural seawater treated with an isothiazolin based biocide at 5 ppm [Gusmano, 2005]. Biocide electrochemical indifference at the employed concentrations was checked (data not shown). In this tank the solution renewal was made every 3-4 days. In B tank the water renewal was made during night hours with slow water feeding and was stopped 1 hour before morning and day-time measurements.

2.2 Electrochemical circuit

Three cuts from a carbon steel bar ϕ=10mm (0.785 cm^2/cut) were short circuited constituting a single cathode with coplanar working faces separated by ~3cm distance. the contacts were insulated with epoxy resin. The surface finishing was performed with a 320 grit paper. Each tank was devoted to contain three triplets: T1, T2, T3 in the biological tank “T”, and TS1, TS2, TS3 in the biologically inactivated tank “BI”. The three cuts composing each triplet were named “a,b,c”.

T and TS triplets series were polarized with two Zn anodes (1 anode/serie) and the potential was controlled in the -850±50 mV Ag/AgCl range through resistors connecting anodes and cathodes. The potential range inducing $i_L O_2$ currents, i.e. -850±50 mV Ag/AgCl, was ascertained with a dynamic scan (1000 mV/h, room temperature). The current densities for each cathode-triplet were computed with the Ohm’s law:

1]: $i = \frac{E_{cat}^{t} - E_{an}}{R} \times \frac{1}{S}$;

where “i” is the current density referring to the whole triplet surface “S” (0.785×3 cm^2), “R” is the resistor connecting the anode to a cathode triplet,” E_{cat}^{t} ” is the cathodic potential of the t-triplet, “ E_{an} ” is the anodic potential.

2.3 Measurements and experiment chronology .

The electrochemical measurements were made in two moments of the day: (1) around 08.00 a.m. in the morning before the direct sunlight hit the tanks (diffuse light time domain, *ante-solem*), (2) around 01.30 p.m. under the zenith hour (direct light regimen, *sub-solem*).

The test was initiated on the 30 June placing both T and TS cathodes-triplets in the biologically inactivated tank BI.

The first two days (1-2 July) the imposed potential was –1000 mV Ag/AgCl in order to induce an initial faster calcareous deposit precipitation. successively, the potential was adjusted at -850±50 mV Ag/AgCl. The 21 July all the T triplets were moved from the biologically inactivated tank BI to the biological tank B, while the TS triplets were kept in the TS tank as controls.

Triplets T2 and TS3 where extracted the 3rd of august (13 days after the separation date of 21 july). Triplets TS1 and T1 where extracted the 9th of august (19 days after the separation date of 21 july). Triplets TS2 and T3 where extracted at the end of the experiment (9th September, 49 days after the separation date of 21 july).

In order to evaluate the sunlight/current interactions, the tanks were artificially obscured. Initially, obscuration lasting 30 minutes was selected. Successively, once ascertained that current response evolved in the first 2 minutes, a 10 minutes time window was used. Full sunny days were selected.

For each triplet, the current drop concomitant to sunlight obscuration was evaluated with a % parameter:

2) $R = \frac{i_{light} - i_{dark}}{i_{light}} \times 100$;

where “i_{light}” is the current density just before the tank coverage, “i_{dark}” is the current density during the tank coverage. R is a measure of the current loss when the tank is obscured: if current still remains the same during tank obscuration (i_{light}=i_{dark}), no loss occurs and R=0%. The photosynthetic active radiation (PAR) flux, $\mu E/m^2 sec$, was determined with a Quantum Sphere Sensor Licor - mod. LI-193SA. This sensor was placed at the electrode depth in the B tank in some days of the 1st half of august.

2.4 surface electrode coverage.

The fouling coverage was evaluated with SEM photographs achieved for each cut composing the cathode-triplet and image analysis was performed (Rasband, 1997-2008). On each cut photographs were obtained on 90 fields (10000 μm^2/field) in order to estimate the % coverage of the biofouling living organism. % coverage were described as mean and standard deviation of the 90 fields belonging to each of the three cuts composing a cathode (3 cathodes, 3 extractions).

3. RESULTS

3.1 From 1 to 21 July.

From 1 to 21 July all the six cathodes (three TS and three T) were polarized in the BI tank in order check sunlight effect on currents beyond a 3 days period, and in order to appreciate biofouling effects on a mature calcareous deposit (once T cathodes are transferred into B tank). fig. 1 shows the path of index R for the current % loss during tank obscuration for the TS cathodes remaining in the BI tank for the entire duration of the experiment. it is clear that sunlight affects cathodic current densities far beyond 70 hours. Particularly, till the last measurements (9th august) the current losses were always appreciable and not larger than ~20%.

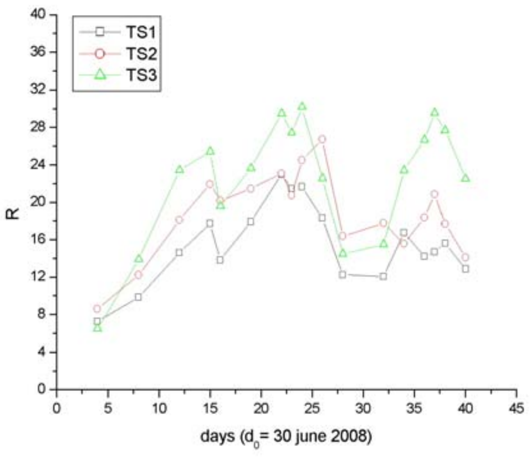

Fig.1: current losses during sunlight obscuration performed across the zenith hour. Here is showed the behaviour of TS cathodes immersed in the tank BI (calcareous deposits effects only).

3.2 From 21 to 26 of July

From the transferring date (21 July) of T triplets from the biologically inactivated tank BI into the biological tank B, three important aspects emerged during the successive days: (1) T current densities fastly dropped and stabilized around 8 $\mu A/cm^2$ while TS controls stayed always at higher values (fig.2); (2) T currents were indifferent to artificial sunlight obscuration and to successive cloud passages, while TS controls reacted in both situations (fig.4, fig.5); (3) the standard deviation of currents measured in the morning before the sunlight direct hit (*ante-solem*) was reduced of almost one order of magnitude, practically disappearing, with respect to the anyhow low standard deviation values showed before the transfer date (fig.3).

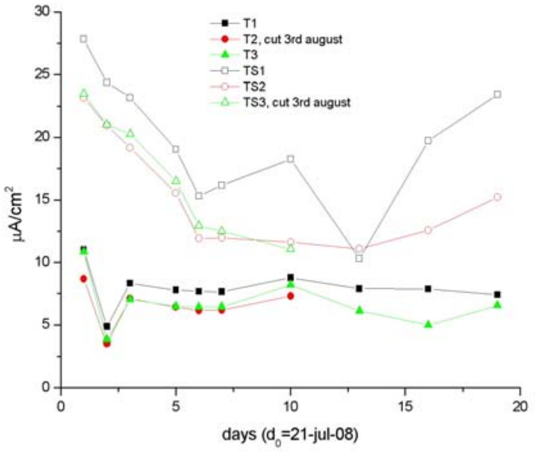

Fig.2: current of T and TS cathodes path when measured in the morning before the sunlight direct hit. Currents are averaged on 30 minutes (1points/2minutes acquisition rate).

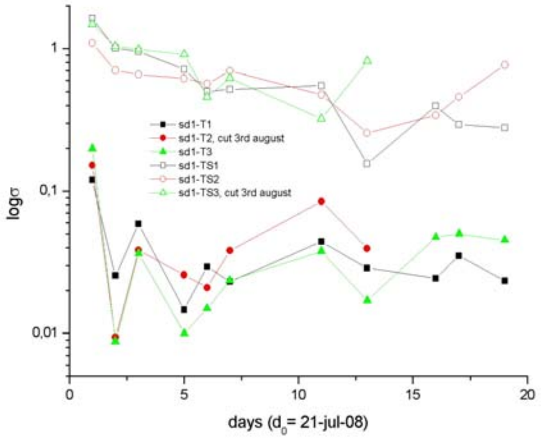

Fig.3 $\log_{10}$ of the standard deviation (logσ) belonging to T and TS currents in the morning before the sunlight direct hit (measurements over 30 minutes, 2points/2minutes acquisition rate) .

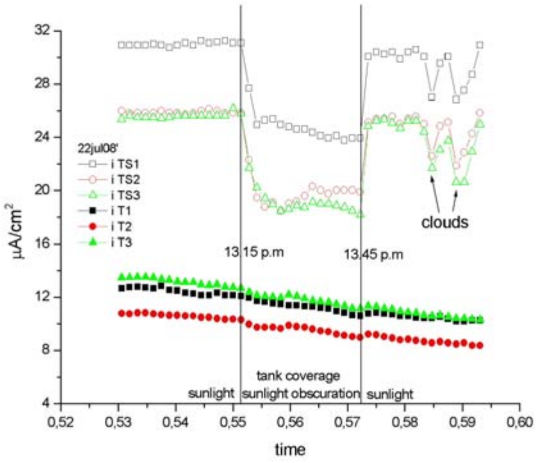

Fig.4: T and TS current drop during both tanks obscuration across the zenith hour the day after T cathodes transfer in the biological tank.

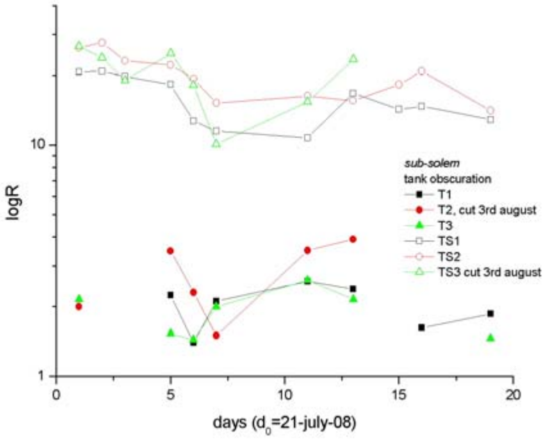

Fig.5: T and TS current drops during tank obscuration across the zenith hour during days successive to the T cathodes transfer in the biological tank.

3.3.1 From 26 of July to 9 of august. Sub-solem tanks obscuration.

As shown in fig.4, the difference in current responses between T and TS cathodes during tanks coverage behaved as follows: for TS control cathodes R was always around 15÷25% during the *sub-solem* tank obscuration, while T cathodes started to be affected with continuity only 6 days after the separation (R~2%). Underwater PAR flux across the zenith hour was measured to be ~1500 μE/cm^{2}sec.

3.4.1 From 26 of July to 9 of august. Ante-solem tanks obscuration.

Along with the zenith hour obscuration, the 3rd of august it was decided to perform tanks obscuration in the morning 1 hour before the direct sunlight hit. So, it was possible to appreciate diffuse lights effects as well.

The T and TS currents behaved as follows: TS controls were completely indifferent to the tank obscuration, while T cathodes lost always around the double of their own loss showed during the *sub-solem* obscurations (see fig.5). Underwater PAR flux in this moment of the day was measured to be ~30 μE/cm^{2}sec.

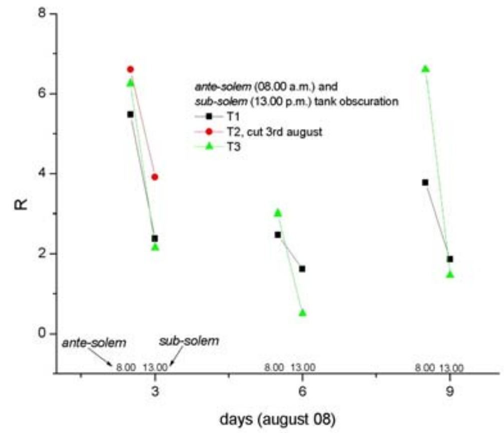

Fig.5 current drop of "T" currents in the morning before the sunlight direct hit (*ante-solem*) and under the zenith hour (*sub-solem*)

3.5 Time evolution of % diatom coverage on T cathodes.

The coverage of living organisms was almost totally represented by diatoms. Fig.9 shows the time evolution of diatoms % coverage of cathodes extracted 13, 19 and 49 days after the T and TS cathodes separation date (21 july). In fig.9, besides the actual data, is showed a region (the white rectangle around the 6th day) where the real data are of lack. Since the literature didn't help us about the time evolution of diatom % coverage, we hypothesized that around a week the diatom % coverage can be thought to be about 20% or 10%, if the colonization is a saturation-like kinetic ("A", top rectangle fig.6) or a sigmoidal-like one ("B", bottom rectangle fig.6) respectively.

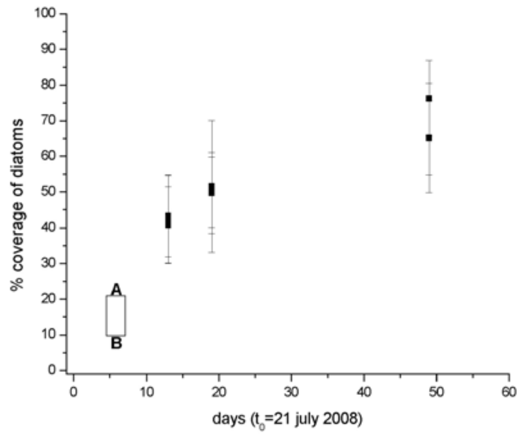

Fig.6: means and standard deviations of % diatom coverage observed on the cathodes extracted 13, 19, and 49 days of immersion in the biological tank. In the white rectangle are typed the expected data (lack of experimental ones) around the first week.

4. DISCUSSION

4.1. from 1 to 21 July.

Previous work [Benedetti, 2009] showed that sunlight affects cathodic current density in absence and in presence of calcareous deposit (3-days field tests). In the research presented here, sunlight effects were evident for the entire duration of the experiment (1 month). The same cited authors hypothesized that the sunlight effect on oxygen limiting currents is related probably to the conversion of sunlight radiation in heat at the metal-solution interface. The presence of calcareous deposit would act as an interference reducing without eliminating this effect.

Therefore, the capability of calcareous deposit in controlling the sunlight effects requires more detailed experiments: particularly, the correlation among calcareous deposit growth, cathodic current density, and light effects has to be characterized.

4.2. from 21 to 26 of July.

Once the T cathodes were transferred into the B tank, important differences were evident just from the day after. These lead to think that something occurred at the calcareous deposit interface. Particularly, the current density and standard deviation decrease during *ante-solem* hour suggested that a layer able to reduce and order the oxygen flux towards underlying polarized metal fastly developed.

The times of such manifestations are compatible with the formation of the “conditioning film”. This layer, which could act as a thin mechanical limiting the oxygen flux from the bulk towards metal, is composed by humic substances, proteins, polysaccharides, nucleic acids, and macromolecules (Garg; 2009). It forms on immerged substrata rapidly and inevitably within minutes-hours (Chambers; 2006). Furthermore, the indifference to sunlight effects exhibited by the T cathodes isn’t in contradiction with the hypothesis of an early developing conditioning film. Indeed, besides reducing and ordering the oxygen flux towards metal, the “conditioning film” can be reasonably thought to intercept the photon flux and prevent current enhancements.

4.3. from 26 of July to 9 of August.

Once the T cathodes were transferred from the BI tank into the B tank leaving TS controls cathodes in the BI tank (21 July), it took no less than 6 days to see i_LO_2 current variations during *sub-solem* tank obscuration. The current decreases encountered in these phases are probably related to the interruption-restoration of the diatom layer photosynthetic activity: when the tank is covered, no radiation hitting diatoms meant interruption of the O_2 production and *vice versa* when the obscuration was removed.

To comment these results it is useful to remind the photosynthesis/irradiance (P/I) curves which are modelled with a saturation kinetic [Platt, 1980].

The most important evidence suggesting diatoms intervening in the O_2 balance at the electrode/solution interface through photosynthesis modifications during tank coverage, is what happens in the diffuse light time domain (08.00 a.m). Here, during tank obscuration, the T cathodes showed current losses, while the TS controls were totally indifferent (fig.5). Literature shows that in presence of a weak PAR flux of ~30 $\mu E/cm^2 sec$ the photosynthetic activity is anyhow stimulated due to a saturation kinetic [Platt, 1980; Post, 1985].

Nevertheless, i_LO_2 loss of T cathodes under *ante-solem* obscuration is generally twice than how measured 5 hours later across the zenith hour (fig.5). A possible interpretation could be related to the photosynthetic inhibition occurring under the highest PAR flux (~1500 $\mu E/cm^2 sec$, zenith hour) [Platt, 1980; MacIntyre, 2002]. Anyway, the photosynthetic activity is a rather complex topic [Hanelt, 1993; Kuhl, 1996; MacIntyre, 2002] and the above advanced assumptions need further characterizations and investigations. Furthermore, O_2 balance modifications reflecting on i_LO_2 fluctuations would undergo attenuation mediated by the underlying conditioning film.

Staying on the hypothesis of a diatom layer participation on i_LO_2 through photosynthetic activity, is clear that a single diatom would provide a negligible contribution, while more diatoms would provide a larger and detectable contribution.

In this sense, it is obvious that a threshold of diatom % surface coverage has to be reached to appreciate a variation in the O_2 balance at the electrode-solution interface and a consequent variation of i_LO_2. The appearance of a *sub-solem* current drop at the 6th day from 21 july lead to think that less than 50% of diatom surface coverage (probably between 10 and 20% depending on the colonizing kinetic) was here required to appreciate i_LO_2 variations (fig.9).

Furthermore, since (1) diatom % coverage data in the first week are of lack, (2) the *ante-solem* obscurations were started the 3 of august (two weeks after T and TS cathodes separation and almost one week after the appearance of *sub-solem* current drop), (3) the *ante-solem* obscuration was revealed to be more sensitive than the *sub-solem* one, it is even more difficult to evaluate the diatom % coverage threshold required to appreciate current losses in the diffuse light domain. This aspect, along with a better characterization of colonization kinetic of the diatoms (% coverage data in the first week) require further investigations.

5. CONCLUSIONS

Cathodic protection in natural photic seawaters was studied polarizing carbon steel electrodes applying oxygen limiting current potential (-850±50 mV Ag/AgCl) with Zn anodes.

In order to separate the calcareous deposit and the biofouling effects, all the cathodes were firstly polarized in tank filled with biologically inactivated seawater for three weeks, thereafter half of the cathodes were transferred in tank filled with renewed natural seawater. The synchronic role of the calcareous deposit growth and the photosynthetic biofouling colonization will be evaluated with further researches. All the polarization tests were performed under natural photoperiod.

Obtained results are resumed as follows:

- In absence of biological effects and in presence of calcareous deposit, sunlight effects were evident along the entire duration of the experiment (1 month).
- with respect to controls, biological cathodes showed just after 1 day (1) lower current values and standard deviation, (2) indifference to the sunlight under zenith hour. The develop of a “conditioning film” able to lower and order the O_2 flux towards metal and to intercept the sunlight is suggested.
- Slight current decreases of biological cathodes observed during sunlight interruptions performed across the zenith hour appeared 6 days after their transfer in the biological tank. Differently, control cathodes losses were evident and larger before and after the transferring date.
- Sunlight interruptions performed in the diffuse light domain (early morning) showed that biological cathodes losses were twice with respect to their own losses under the zenith hour sunlight interruptions, while controls were totally indifferent.

Finally, in our experimental conditions (shallow photic seawaters), the biological component developing on previously grown 3 weeks calcareous deposit, was characterised as follows: a mere passive function was performed probably by the conditioning film (most important effects) preventing sunlight induced enhancement of the current. Diatoms, constituting the larger fraction of colonizing organisms, played an active effect through photosynthetic activity. This effect was revealed to be of slight importance, probably because of the mediation of the underling conditioning film. Diatoms passive effect appeared to be negligible.

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