

# THE EFFECT OF AERATION ON THE CORROSION PROCESS OF MAGNETIZED Nd-Fe-B MAGNETS

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## Abstract

The effects of aeration upon the corrosion process of magnetized Nd-Fe-B based sintered magnets have been studied. The tests were carried out in naturally aerated and in deaerated 3.5 (wt.%) sodium chloride solutions at various testing times by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization methods. In deaerated solution the magnets exhibit higher impedance values (one order of magnitude) than in aerated one. Bode phase angle diagrams obtained in the former solution presented a single broad time constant, indicating the existence of a single process in the investigated frequency range; moreover, the impedance behaviour was maintained fairly constant from 5 days of immersion throughout the rest of the testing period. On the other hand, the sample immersed in the aerated solution presented a constant and slow diminution of the impedance all long the immersion time. In this case, Bode phase angle diagrams presented a HF shoulder interpreted as the influence of the magnetic field on the transport of oxygen to the interface. Larger  $i_{corr}$  values and more noble potentials were also obtained for the magnet in aerated solution. In the presence of oxygen, the corrosive attack penetrated deeply into the specimens and, consequently, the magnetic properties diminished with immersion time. The magnetic properties most influenced by corrosion were the remanence ( $B_r$ ) and the maximum energy product ( $BH_{max}$ ).

## 1. Introduction

It is well known that corrosion reactions yield magnetic fields. The first attempts to study magnetic fields resulting from in-situ corrosion, nearly two decades ago, were carried out by Bellingham et al [1, 2]. Recently, Juzeliunas and Hinken [3] examined the correlation between corrosion currents and magnetic fields using a SQUID (superconducting quantum interference device) magnetometer and concluded that the corrosion reaction yielded magnetic fields. Since corrosion currents are small, the intensities of any associated magnetic fields are also expected to be low and should not affect the corrosion process. The intensities of magnetic fields resulting from corrosion reactions determined by SQUID investigations reached values of several nano-Tesla [4-6]. However, it should be expected that an external magnetic field would affect the internal currents and, hence, the corrosion rate should differ from that in field-free environment.

Although the literature [7-9] reports that the magnetic field affects the corrosion process, the results presented are contradictory. Some authors concluded that the effect of this variable is beneficial, causing the decrease in the corrosion rate [7,9], whereas an accelerating effect on the corrosion process has also been reported [4]. Many reasons for this have been pointed out [10-14], such as the effect of the magnetic field on mass transport [13, 14]. The aim of this study was to evaluate the effect of aeration on the corrosion process of magnetized commercial Nd-Fe-B permanent magnets. The tests were carried out in naturally aerated and deaerated 3.5 (wt.%) sodium chloride solutions.

## 2. Experimental Procedure

Commercial sintered Nd-Fe-B magnets produced by Crucible were used in this investigation. The composition determined by X-ray fluorescence analysis and atomic absorption measurements is given in Table 1. The corrosion behaviour of the magnets was investigated in naturally aerated and deaerated 3.5 (m/v)% NaCl solutions. In all the tests, solutions were quiescent and the temperature was in the range of  $(23 \pm 2)$  °C. Corrosion tests were performed with magnetized and non-magnetized samples. Magnetization was carried out up to saturation in a pulsed field of 6 T.

Table 1. Chemical composition of commercial Nd-Fe-B magnets.

Elem	Fe	Nd	B	Dy	Al	Co	Si	Cu	Nb
wt.%	60.9	28.6	1.0	2.1	3.8	1.3	1.4	0.2	0.7
at.%	67.9	12.3	5.8	0.8	8.1	1.4	3.1	0.2	0.4

Electrodes with an approximate transversal area of 130 mm<sup>2</sup> were prepared by cold resin mounting. Before testing, they were ground with silicon carbide paper up to grade #1000, followed by degreasing with acetone, using an ultrasonic bath, rinsing with deionized water and drying under a hot air stream. Magnetization was carried out after surface preparation. A three-electrode cell arrangement was used for the electrochemical measurements, with a graphite rod and saturated calomel (SCE) as counter and reference electrodes, respectively. Electrochemical impedance spectroscopy (EIS) measurements were accomplished with a 1255 Solartron frequency response analyzer coupled to an EG&G 273A Potentiostat. All EIS experiments were performed in potentiostatic mode at the corrosion potential ( $E_{corr}$ ). The amplitude of the perturbation signal was 10 mV, and the investigated frequency range varied from 10<sup>5</sup> to 10<sup>-2</sup> Hz with an acquisition rate of 6 points per decade. Potentiodynamic polarization measurements were carried out using an EG&G 273A Potentiostat coupled to a computer. The investigated potential range was from -1300 mV (SCE) to 0 mV (SCE) at a scan rate of 1 mV/s. Electrochemical measurements were obtained at increasing test times, from 1 until 30 days of immersion. The magnetic properties of specimens, before and after testing in naturally aerated solution, were determined in a permeameter. Measurements were performed after saturation in a pulsed field of 6 T.

## 3. Results and Discussion

Figure 1 shows the impedance response for the Nd-Fe-B magnets at increasing immersion times in deaerated chloride solution. These diagrams show that in the absence of oxygen in the solution the magnet impedance increases from the first to the fifth day of immersion, and then maintains a fairly constant behaviour throughout the rest of the experiment period. The initial increase in the impedance values can be probably explained by the removal of more active phases from the electrode surface during the first days of contact with the aggressive electrolyte. Indeed, for the magnets used in this study (with Nd-rich phase and porosities) the preferential attack of these more active regions would result in a cleaner surface exposed to the electrolyte improving the corrosion resistance. The very low oxygen content in the test solution must be responsible for the stabilization of the corrosion process for longer immersion periods.

Bode phase angle diagrams presented in Figure 1 show a single broad capacitive time constant, indicating the existence of a single process in the investigated frequency range. The flattened appearance of this time constant can be likely ascribed to the porosity on the magnets surface (as consequence of fabrication by powder metallurgy) and also to the corrosion process. Upon increasing the immersion time, a slight increase in the high frequency phase angle can be observed, this can be related to pore blocking by corrosion products diminishing the surface porosity, which would move the electrode behaviour towards that exhibited by a flat one.

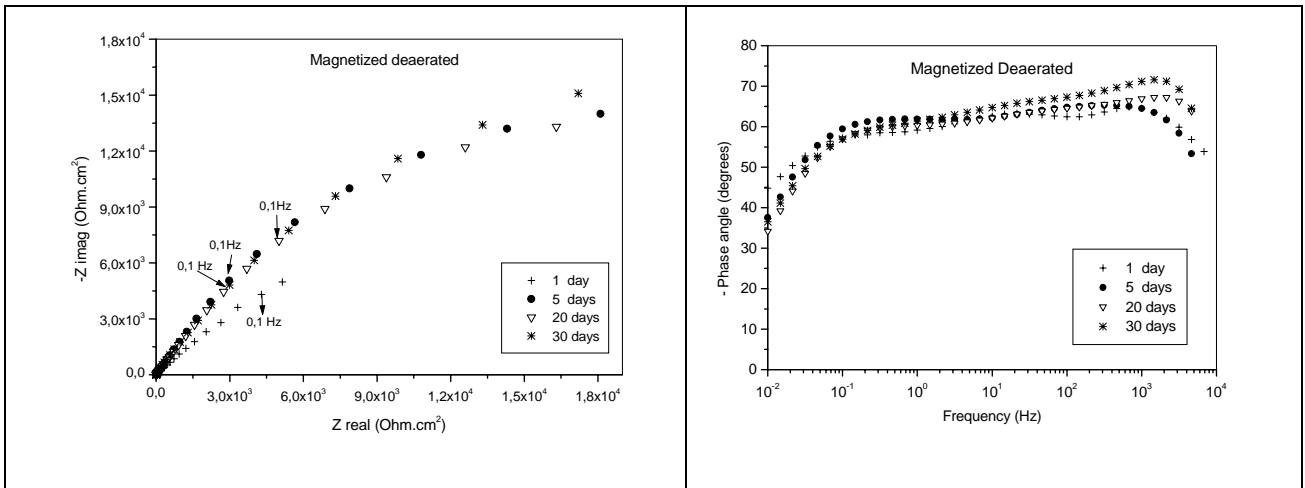


Fig.1. Nyquist and Bode plots for magnetized Nd-Fe-B specimens at increasing immersion times in deaerated 3.5 (wt.% ) NaCl solution.

As can be seen in Figure 2, the sample immersed in the aerated solution presented a constant and slow diminution of the impedance response all long the immersion time, indicating an important role played by this aggressive specie on the corrosion process. The behaviour of this sample is characterized by a steep decrease of the low frequency phase angle indicating a fast interfacial kinetics. Moreover, Bode phase angle diagrams show the presence of a small high frequency (HF) shoulder that is gradually displaced to lower frequencies for increasing immersion time, which significance will be discussed later.

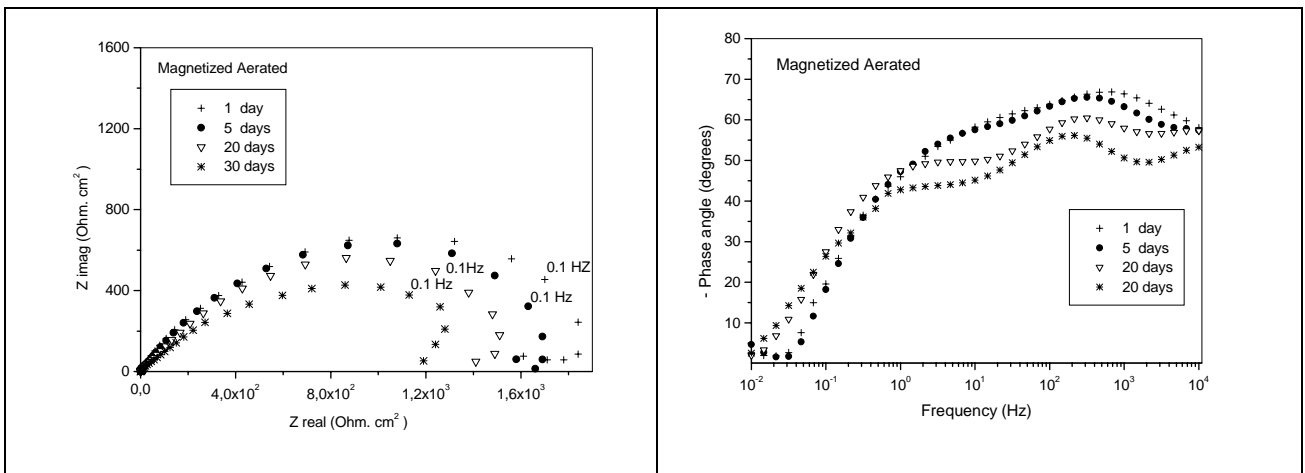


Fig.2. Nyquist and Bode plots for magnetized Nd-Fe-B specimens at increasing immersion times in aerated 3.5 (wt.% ) NaCl solution.

A comparison of Bode phase angle diagrams for aerated and deaerated samples is shown in Fig. 3. The diagrams suggest that the corrosion mechanism must be different according to the presence or absence of oxygen in the electrolyte, and clearly shows higher impedance values for the electrode immersed in the deaerated, particularly for longer immersion periods. This better behaviour was further confirmed by the results obtained in the potentiodynamic experiments where the corrosion rate ( $i_{corr}$ ), estimated from the polarization curves by extrapolation of linear segments of the cathodic branches to the corrosion potential,  $E_{corr}$ , was 4-fold higher for the electrode immersed in the aerated solution. This response was associated with nobler  $E_{corr}$  for this latter sample. In addition, SEM images presented elsewhere [19] show the presence of a crevice network on the surface of the samples after immersion in aerated and deaerated solution, however, deeper crevices were formed on

the surface of the sample immersed in the former solution, as stronger corrosive attack was verified. For aerated solution, Bode phase angle diagrams are flatter than those obtained in deaerated one, and the angle steadily decreases for longer immersion time approaching the 45° behaviour associated with porous electrodes [18]. This behaviour can be explained by porosity increasing of the magnet surface due to the presence of adhered magnetic particles (iron rich magnetic phase) and corrosion products. These products would difficult the access of the electrolyte to the electrode surface giving rise to the onset of diffusion controlled phenomena. The adhered products would also reduce the magnetic properties of the sample influencing the bulk transport of dissolved oxygen.

As previously mentioned, in aerated solution dissolved oxygen must play a significant role in the corrosion process along the whole test period. The Bode diagrams for the sample in this solution revealed the existence of a high frequency feature (a small shoulder), which is absent in the deaerated solution. It has been previously proposed [16] that this time constant must be related to the influence of the magnetic field on bulk oxygen diffusion (due to the paramagnetic properties of this molecule [17]) accelerating the interfacial corrosion process. The formation of the crevice network with immersion time would hinder the transport of oxygen to the magnet surface displacing the time constant associated to this process, the HF shoulder, to lower frequencies, as can be seen in Figure 2.

Fig. 3 also shows a comparison of EIS diagrams for both types of sample for periods longer than five days. The impedances of the sample in deaerated solution is one order of magnitude higher than in aerated one, as a consequence of the lower aggressiveness of the deaerated solution.

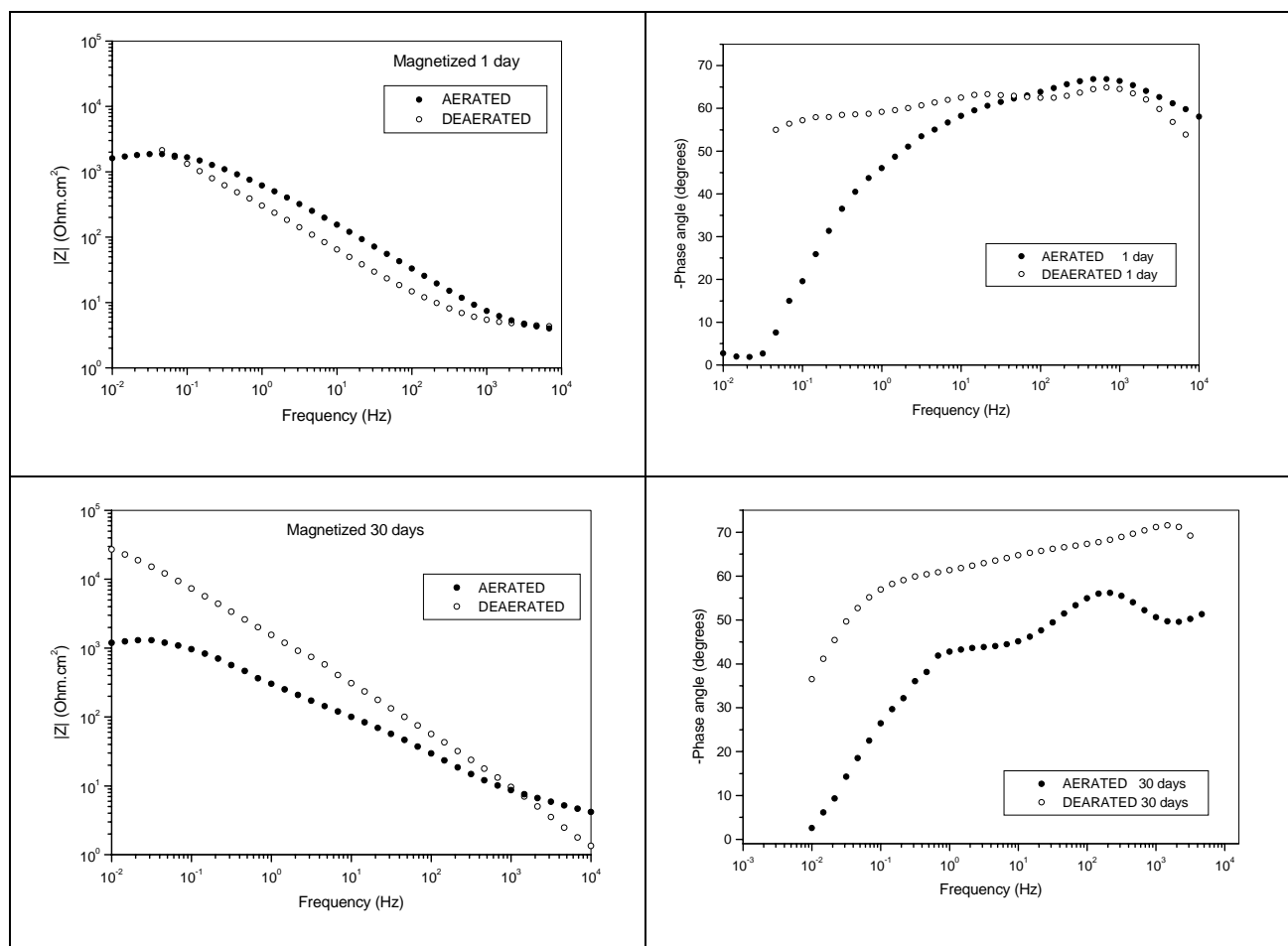


Fig.3. Bode plots for magnetized specimens in naturally aerated and deaerated solutions after 1 day and 30 days of immersion. Electrolyte: 3.5 (wt.%) NaCl solution.

The demagnetization curves of the Nd-Fe-B samples were determined before and after increasing periods of immersion in the naturally aerated chloride solution and the results are shown in Fig. 5. A

degradation of the second quadrant loop was observed with increasing immersion time. The magnetic properties most influenced by corrosion are the remanence and the maximum energy product, with values that varied from 1.22 T to 1.15 T, and from 293 to 275 kJ.m<sup>-3</sup>, respectively (a reduction of around 6%).

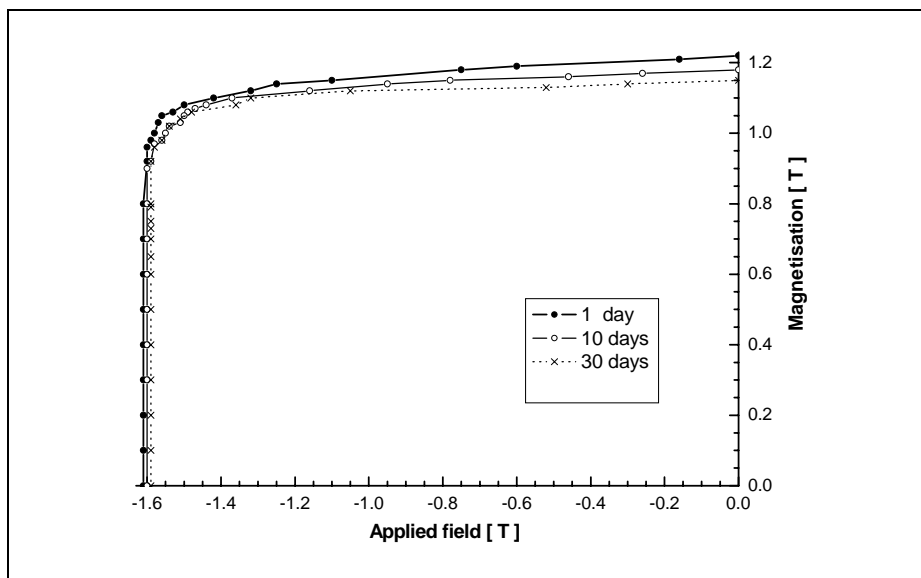


Fig. 5. Demagnetization curves for 1 day, 10 days and 30 days of immersion in naturally aerated 3.5 wt.% NaCl solution.

#### 4. Conclusions

The results here presented show that aeration has a significant effect on the electrochemical response of magnetized Nd-Fe-B samples. The electrochemical impedance response for the sample in aerated solution revealed the existence of a high frequency time constant that was associated to the influence of the magnetic field on bulk oxygen diffusion, due to the paramagnetic properties of this molecule accelerating the interfacial corrosion process. The impedances of the sample in deaerated solution is one order of magnitude higher than in aerated one. The results show that the magnetic properties most influenced by corrosion were the remanence and the maximum energy product, both presenting a reduction around 6%.

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#### 6. References

- [1] J. G. Bellingham, M.L.A. MacVicar, M. Nisenoff, P.C. Scarson, *J. Electrochem. Soc.* 133 (1986) 1753
- [2] J. G. Bellingham, M.L.A. MacVicar, M. Nisenoff, *IEEE Trans. Magn.Mag.* 23 (1987) 477.
- [3] Eimutis Juzeliunas, Johann H. Hinken, *Journal of Electroanalytical Chemistry* 477 (1999) 171-177
- [4] A.D. Hibbs, *IEEE Trans. Magn. Mag.* 139 (1992) 2447
- [5] D. Li, Y. Ma, W. F. Flanagan, B.D. Lichter, J.P. Wikswo Jr., *Corrosion*, 53 (1997) 93
- [6] E. Juzeliúnas, J.H. Hinken, *J. Electroanal. Chem.*, 477 (1999) 171.
- [7] A. Rucinskiene, G. Biculsius, L. Gudaviciute and E. Juzeliunas, *Electrochem. Comm.* 4 (2002) 86.

- [8] M. Sagawa, Trans. Japan Inst. Met. **23** (1982) 38.
- [9] A. Chiba, N. Tanaka, S. Ueno, T. Ogawa, Corros. Eng. **41** (1992) 333.
- [10] E. J. Kelly, J. Electrochem. Soc. **124** (1977) 987.
- [11] J. Chopart, J. Douglade, P. Fricoteaux, A. Olivier, Electrochim. Acta **36** (1991) 459.
- [12] A. Chiba, K. Kawazu, O. Nakano, T. Tamura, S. Yoshihara, E. Sato, Corros. Sci. **36** (1994) 539.
- [13] K. Shinohara, R. Aogaki, Electrochemistry **67** (1999) 1261.
- [14] V. Novinski, Electrochim. Acta **42** (1997) 251.
- [15] H. Bala, S. Szymura, Corr. Sci., 32 (1991) p.953.
- [16] I. Costa, M.C.L. Oliveira, H.G. de Melo, R.N. Faria, J. Magn. Mag. Mater, *in press*.
- [17] T. Sasada, A. Sato, Physics Letters A 266 (2000) p.350. [17] T. Sasada, A. Sato, Physics Letters A 266 (2000) p.350.
- [18] R. de Levie, Adv. Eletrochem. Eng. 6 (1967) p.329.
- [19] M.C.L. Oliveira, M.Sc. dissertation, University of Sao Paulo, Brazil, 2004.

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