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The study of corrosion through the Mössbauer effect is a small step towards a sustainable development in harmony with nature

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Abstract. In the introduction, brief considerations about sustainable development and harmony with nature are presented. The basic part of the work is divided into 2 parts. In the first part, the technical developments are presented to perform the study of corrosion by the Mössbauer effect. To carry out these studies, the four types of proportional detectors were developed. In the second part, the results obtained in the study of corrosion through the Mössbauer effect are presented, mainly on low-alloyed carbon steel samples. The corrosion products formed on such a sample after storage in the ambient atmosphere are described and identified. In the study of corrosion processes, the corrosion of low-alloy steel was followed in dilute ammonia media with or without corrosion inhibitors, corrosion of low-alloy steel in dilute HCl solutions with or without corrosion inhibitors. Also the corrosion of stainless steel in physiological environments was addressed. In some studies, the Mössbauer data were supplemented with those obtained by X-rays.

Keywords: Mössbauer effect, carbon steel, corrosion products, corrosion inhibitors, ammonia media, hydrochloric acid solutions, physiological environments.

1. Introduction

Sustainable development was first defined in the 1987 Brundtland report of the World Commission on Environment and Development entitled "Our Common Future" as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs". [1], [2]. At the same time, the Brundtland Report admitted that economic development cannot be stopped, but that strategies must be changed to fit the ecological limits offered by the environment and the planet's resources. A sustainable society is a society that shapes its economic and social system so that global natural resources and life

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support systems are maintained. In 2015, during the work of the UN summit in New York, the 2030 Agenda for sustainable development was adopted. Through this document the UN has provided a universal agenda with clear and quantifiable objectives. The 2030 Agenda includes a set of 17 Sustainable Development Goals (SDGs) and an action plan for the next 15 years, to eradicate extreme poverty, combat inequalities, injustice and protect the planet by 2030 [3]. Romania, as a member state of the United Nations (UN) and the European Union (EU), expressed its adherence to the 17 Sustainable Development Goals (SDGs) of the 2030 Agenda.

The conclusions of the EU Council, adopted on June 20, 2017, "A sustainable future of Europe: the EU's response to the 2030 Agenda for Sustainable Development" represent the political document assumed by the EU member states, including Romania, regarding the implementation of the 2030 Agenda for Sustainable Development. For the implementation of the European provisions and those of the UN documents in the matter of sustainable development, the Department for Sustainable Development was established, by Government Decision no. 313/2017 [3]. The department operates within the working apparatus of the Government, subordinated to the Prime Minister, financed from the state budget through the budget of the General Secretariat of the Government. Through this Department, Romania establishes its national framework for supporting the 2030 Agenda and implementing the set of 17 SDGs. The Department's strategy supports Romania's development on three main pillars, namely economic, social and environmental. The strategy is citizen-oriented and focuses on innovation, optimism, resilience and confidence that the state serves the needs of every citizen, in a fair, efficient and clean environment, in a balanced and integrated way.

Living in harmony with nature is very important, first we must know that we ourselves are nature, if we destroy it we destroy ourselves. Nature is also a good remedy against melancholy, when you feel alone and you can't even call on your best friends, and then only nature can help you. We must live in harmony with nature because it gives us natural resources, raw materials and food. We have to get along perfectly with nature because if it doesn't exist then we will disappear too. We must protect nature, not just love it, because words without deeds are nothing, so the next time you have contact with nature, remember that you are a part of it and our life on earth is due to Nature. There is a huge literature on the relationship between man and nature. From it I will mention 10 interesting ideas about how we can be in harmony with nature: walk in nature, pay attention to details, free your mind, meditate in nature, do sports in nature, photograph nature, slow down and just "be present" , use every sense, choose a place to sit, learn the names of some plants [4].

Under ambient conditions a metallic material forms compounds by reactions with the medium contacted. While “corrosion” describes the degradation of a material the by chemical reactions with the surrounding medium, in particular “rusting” describes the corrosion process of iron-based materials by reactions with water or humid air including the presence of solved and polluted solvents [5]. Natural corrosion is, most commonly, an undesirable process by which many metals with positive or slightly negative oxidation potentials are transformed into their chemical compounds. Well-known and particularly damaging to the economy is the rusting of iron. A significant part of corrosion occurs in the total absence of oxygen. To understand and to reduce the corrosive attack on metallic materials is an important task from economical point of view. The annual worldwide cost of metal corrosion is estimated to be over 2 trillion dollars, but experts believe that 25 - 30% could be prevented with proper corrosion protection [6]. Corrosion is a waste of natural resources and can lead to safety issues, loss of life, etc.

Mössbauer spectroscopy is, among others methods, a very valuable tool to study the corrosion process. Mössbauer spectroscopy [7] (or nuclear γ resonance) is based on the incorporation of the emitting and absorbing nuclei within a solid matrix, which enables resonant recoil free absorption and emission of γ -rays. Its importance lies in the very narrow line width of the emitting photon and the consequent ability to probe the variations in nuclear energy levels resulting from any discrete changes in the chemical state and/or environment of the Mössbauer nucleus. Such changes in nuclear energy levels are measured by modifying the energy of the probing γ -rays by applying a Doppler shift: a Mössbauer spectrum therefore consists of a plot of counts against applied Doppler velocity (positive and negative), the velocities corresponding to the addition and subtraction of Doppler energy shifts to the γ -ray energy. Significant recoil-free-fractions occur only for gamma energies less than 150 keV. This fact obviously means that room or high temperature Mössbauer work is possible only for a limited number of elements-isotopes, (e.g. ^{57}Fe , ^{119}Sn , ^{151}Eu). Following resonant absorption of a gamma ray, the nucleus may de-excite by emission of a gamma ray or by the process of internal conversion where an inner (K or L) shell electron is emitted. Accompanying conversion electron emission is a characteristic X-ray emitted as a result of the repopulation of the inner energy levels. Detecting the three backscattered particles, permits surface studies to be performed. The electron signal is quite high for the ^{57}Fe , ^{119}Sn and ^{151}Eu isotopes. The ^{57}Fe isotope is the most studied isotope; over 60% from publications are dedicated to iron. One of the most important features of Mössbauer spectroscopy is the ability to simultaneously perform volume and surface analyses. It is a non-destructive technique that can be applied in situ to investigate surfaces of variable thickness from thin films to coatings without the need to remove them from their substrate. It allows a chemical, structural and magnetic characterization through a single experiment and can examine surfaces and interfaces at a local atomic scale.

In this paper the results obtained in the study of corrosion through the Mössbauer effect, mainly on low-alloyed carbon steel samples, in different media (diluted

ammonia/ammonium solutions, dilute HCl solutions, artificial physiological environments) are presented. Also the effect of some organic inhibitors on the corrosion in the mentioned media was studied. The technical developments to efficiently and accurately perform the study of corrosion by the Mössbauer effect were performed,

2. Experimental

I performed the first study on corrosion by Mössbauer effect at the suggestion of professor of physics from my faculty, Prof. Dr. G. Moisil [8]. This first study, carried out in the transmission geometry, showed that in order to obtain relevant and precise data it is necessary to carry out surface studies. Thus, over time, detectors were made for surface studies through the Mössbauer effect and then I made various collaborations for Mössbauer surface measurements.

Were realized 4 proportional counters for conversion Mössbauer spectroscopy: detectors for conversion electron and transmission Mössbauer spectroscopy [9] - [11], toroidal detector for conversion X-ray and transmission Mössbauer spectroscopy (CXMS) [12], [13], detector assembly for simultaneous conversion electron, conversion X-ray and transmission Mössbauer spectroscopy [10], versatile flow-gas proportional counter for electron detection, X-ray detection or transmission measurements function of geometry and used gas [14]. All detectors are flow-gas type and operating at room temperature. Their construction permits for all detectors to realize simultaneous transmission and conversion measurements. The background due to photoelectrons is minimized by using low-Z materials as much as possible. The sample holder allows an easy manipulation of a sample, outside the detector and sample can always be repositioned in a reproducible manner with respect to the detector body. We have used for detectors an economical shielding which consists of a combination of lead, copper and steel disks. To destroy the characteristic radiation, alternate mounting of the lead, copper and steel disks were used. In order to absorb unfavourable KX-rays from the source, a plexiglas filter is placed in front of the shielding.

We constructed flow-gas proportional counters for resonance electrons using two variants to dispose the anode wire: an exterior circle around the sample, and lines in front of the sample. The second variant has better performance. The test measurements argue the versatility of these counters for the comparative study of surface and bulk properties of Mössbauer samples.

The proportional detector for conversion X-ray and transmission Mössbauer spectroscopy [12] has toroidal shape of the space detection and a lower efficiency for the 14.4 keV r-rays. The resonance effect can be optimized by a proper choice of the anode voltage and the filter. The design is simpler than those previously reported for similar devices and is presented in figure 1.

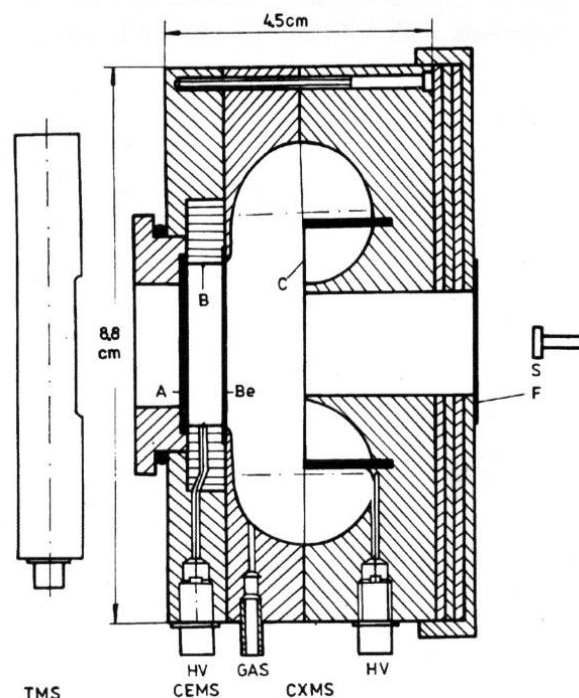


Fig. 1. The detector assembly for simultaneous conversion electron, conversion X-ray and transmission Mössbauer spectroscopy

S: radioactive source; F: filter for X-ray; A: sample; Be: berilium window; B: anodic wire for electrons;

C: anodic wire for X-ray; HV: high voltage connectors; înaltă tensiune; GAS: gas input/output; CEMS: electrons detector; CXMS: X-ray detector; TMS: gamma ray detector

The detector assembly [10] for simultaneous conversion electron, conversion X-ray and transmission Mössbauer spectroscopy consists mainly of two gas-flow proportional counters combined together and is represented in figure 1. The sample to be studied is mounted inside the smaller counter designed for detecting electrons backscattered from the sample. The larger counter, toroidal shape, is used to detect conversion x-rays that come from the sample and pass through the electron counter. This assembly has a low efficiency for backscattered 14.4 keV γ -rays. The counter design and operation are simpler than previously reported.

The versatile flow-gas proportional counter for surface Mössbauer spectroscopy [14] represent a synthesis of my experience in the development of flow-gas proportional detectors for surface studies. The main improvements obtained by new design are: the height of the detection volume can be changed in large limits from 1 to 38 mm, the detection volume can be choose symmetrical or not in respect with anode plan, the anode changing is easily and different anode configuration can be used. By changing the volume detection and flow gas it is possible to make, inside, measurements by electron, X-ray detection or gamma-ray detection. The diagram of this detector is present in figure 2.

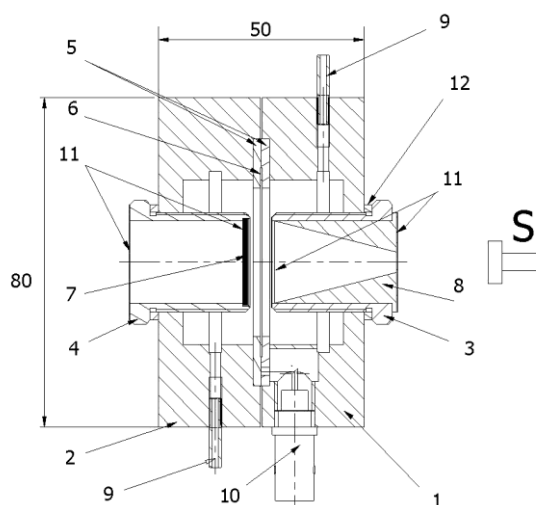


Fig. 2. The cross section of the versatile flow-gas proportional counter, 1 and 2 main parts of the counter, 3 input piece, 4 sample holder, 5 teflon insulator, 6 anodic ring, 7 sample, 8 collimator, 9 gas connection, 10 high voltage connector, 11 mylar windows, 12 tightness piece, S Mössbauer source

3. Corrosion studies

Corrosion studies were performed on low-alloyed carbon steel samples or stainless steel samples used in biological implants. Before being subjected to corrosion studies, the samples kept in the ambient atmosphere are subjected to a complex cleaning process. The media used in the studies were: ambient atmosphere, diluted ammonia/ammonium solutions, dilute HCl solutions, physiological environments. The ^{57}Fe Mössbauer spectra were obtained with a $^{57}\text{Co-Rh}$ radioactive sources and a conventional constant-acceleration spectrometer (AME-50 Elscint). The velocity range was calibrated with $\alpha\text{-Fe}$ standard foil. Lorentzian line shapes were considered to fit the recorded Mössbauer spectra. All isomer shifts are given relative to that of alpha-Fe at room temperature.

3.1 Corrosion products formed on a sample after storage in the ambient atmosphere

The surface of low-alloyed carbon steel sample was studied before the cleaning process [15].

Mössbauer effect measurements were performed in two geometries: transmission (TMS) and backscattering. An absorber from surface of the sample was obtained by scrapping. Information about samples surfaces was found in the backscattering geometry by detecting the conversion electrons (CEMS) and the conversion X-rays (CXMS). The electrons penetration depth is of the order of 250 nanometers and the X-rays penetration depth is of the order of 11 microns [μm]. The backscattering measurements were conducted at a high degree of accuracy with a new detector,

gas-flow proportional [14]. In CXMS measurements, a filter from aluminized mylar with 2.5 microns thickness was used to eliminate the conversion electron signal.

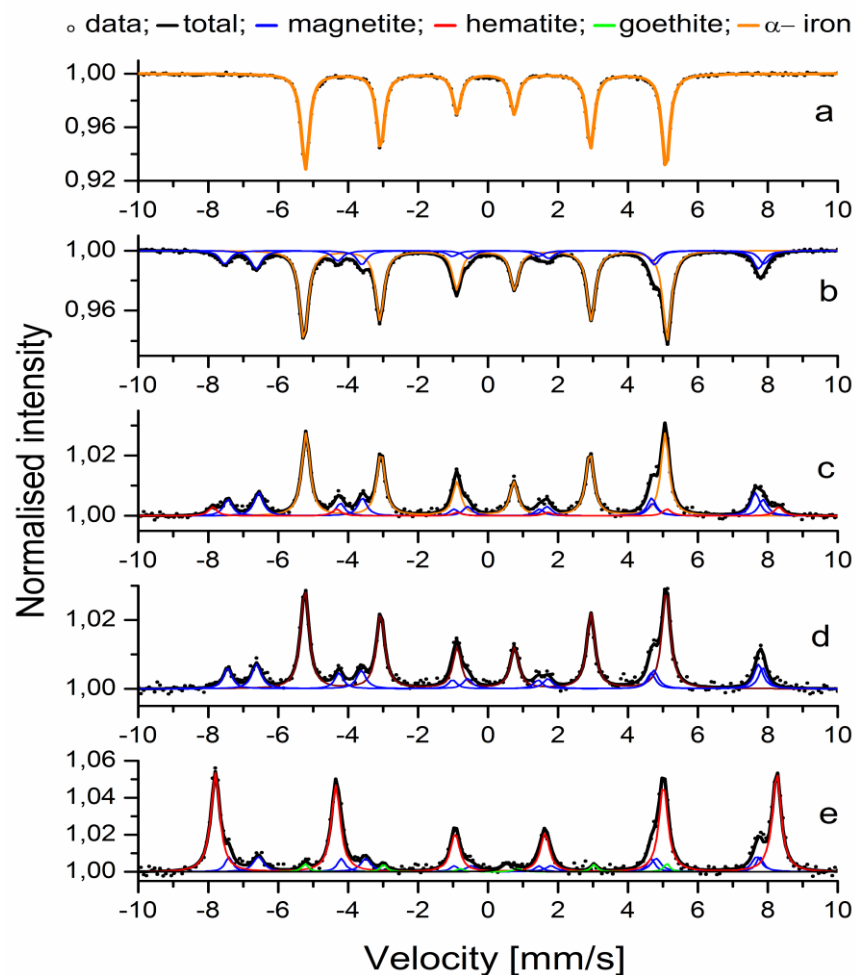


Fig. 3. Mössbauer spectra of the initial sample
(a) from bulk; (b) of surface scrapped layer; (c) by CXMS without filter;
(d) by CXMS with filter; (e) by CEMS

Figures 3 show the Mössbauer spectra of the sample together with the computer fit (continuous lines). The bulk transmission (Fig. 3a) spectrum was fitted with a single sextet due low carbon content. The line width of the outermost lines confirms the low concentrations of alloying elements.

The surface measurements on initial sample prove a marked corrosion: a coating with a considerable thickness and a complex composition. Hematite is the main compound of the outermost layer (Fig. 3e). Its Mössbauer parameters are

practically the same with those given in literature. The second compound in the outermost layer is magnetite with a normal stoichiometry as in different references. The reduced hyperfine magnetic field of goethite compared with well-crystallized goethite (around 380 kOe), can be generally assigned to varying crystallinity of goethite and/or small particles. Poor crystallinity and substitution may modify the spectrum of goethite to such an extent that characterization must be carried out at low temperatures. According to the level diagram of Gibbs free energies of formation for some corrosion products of iron, α -FeOOH is a level in the transition to α -Fe₂O₃. Also a corrosion product can exist in the outermost layer at sensibility limit of the method. Its presence is suggested by smoothing the spectrum. CEMS spectra indicate a corrosion layer thickness greater than 250 nm. The spectrum of steel substrate was not evidenced.

The surface spectra obtained by CXMS without electron filter (Fig. 3c) give the integral information about superficial corrosion layer. The magnetite and hematite are the compounds of the layer. Magnetite is now the main compound of the corrosion layer. The using of the electron filter hides the hematite presence (Fig. 3d). Also the hematite is not present in the surface sample collected by scape method (Fig. 3b). The data obtained for sample collected by scape method are very closely to those obtained by CXMS with electron filter. All CXMS spectra evidenced the steel substrate.

The results of all Mössbauer measurements show the presence of a corrosion layer on steel sample. The layer compounds are magnetite, hematite, and goethite. The relative concentration in increasing order is: goethite, hematite, and magnetite. The goethite and hematite are located at the surface of corrosion layer. We estimated the corrosion layer thickness around 5 microns.

The X-ray diffractograms of the sample confirm the Mössbauer data. The diffractograms consists in two prevailing phases – magnetite and hematite accompanied by small goethite phase as a result of corrosion processes. The α -Fe peak at 45° given by the steel substrate can be also observed.

3.2 Corrosion in diluted ammonia/ammonium solutions

Researchers have commonly ignored the industrial and residual waters containing ammonia/ammonium regarding them as non-dangerous in terms of corrosion. Relatively recent researches, however, have showed such waters have a negative impact on the environment leading to pipe corrosion in the cooling waters systems, especially in the ammonium fertilizer industry. The samples were corroded in a standard electrolytic cell with the followings diluted ammonia/ammonium solutions: diluted ammoniac solutions with NH₃ concentration of 10⁻¹ M, 10⁻² M, 10⁻³ M and 10⁻⁴ M [16], ammonium salts solutions: 0.1M NH₄Cl, 0.1M NH₄Cl with 0.05M NH₄NO₃, [17], solution 10⁻³M NH₃ with 510⁻³M NH₄Cl [18]. The CEMS spectrum of the sample corroded in solution with 10⁻³ NH₃ concentration [16] is shown in figure 4.

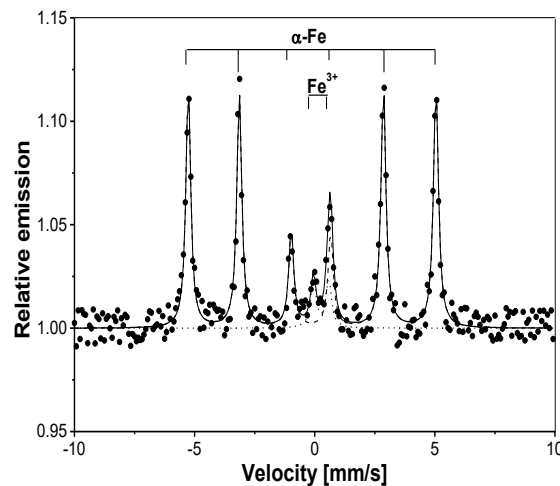


Fig. 4. CEMS spectrum of a Fe-C steel sample corroded in a solution with 10^{-3} NH_3 concentration (• data; — fit; ... Fe^{3+} ; --- $\alpha\text{-Fe}$)

The best fit of the CEMS spectrum for the corroded sample uses an addition Fe^{3+} paramagnetic doublet to the sextet. The parameters of the sextet (hyperfine magnetic field, quadruple splitting, isomer shift, line width) are almost identical to those of the non-corroded sample. The slight changes of the hyperfine magnetic values and isomer shifts suggest that in the process of corrosion there may be a certain preference for the positions of iron, which are not close to the atoms of the alloying elements. The preferential orientation of the magnetic moments in the sample plane continues to exist even after the corrosion of the samples. The main difference between the corroded sample sextets and the non-corroded sextets consists in the decrease of the intensity lines corresponding to $\alpha\text{-Fe}$. This demonstrates, once again, the presence of a superficial layer on the corroded samples surface. There is a process of inhibition of carbon-steel corrosion in the ammoniac solutions, which is evidenced by the increase of the superficial layer when NH_3 concentration decreases. The parameters of the doublets show the presence of Fe^{3+} and are similar to those shown by amorphous Fe^{3+} oxyhydroxides, superparamagnetic $\alpha\text{-FeOOH}$ and/or $\gamma\text{-FeOOH}$ and $\text{Fe}(\text{OH})_3$. Small relative area of the doublet, as well as its parameters shows the initial stage of the corrosion. At this stage we believe that the main product of the corrosion in NH_3 solution is an amorphous Fe^{3+} oxyhydroxide with a non-stoichiometric composition. Mössbauer data showed that for the samples corroded in ammonium salts solutions the main corrosion product is a mixture of Fe(III) ferrihydrate and FeOOH (alpha and/or gamma). The introduction of NO_3^- anion in a solution of 0.1M NH_4Cl in $\text{NO}_3^-/\text{Cl}^- = 1/2$ ratio has an inhibiting effect by decreasing the expansion rate of generalized corrosion of carbon steel. This effect is demonstrated by the increase of the sextet lines intensity and the dramatic decrease of the Fe^{3+} paramagnetic doublet.

Numerous advanced treatments using organic compounds have been proposed in order to improve the corrosion protection. The inhibition effect of three organic compounds: 2-mercapto-benzothiazol (MBT) [19], N-ciclohexil-benzothiazole-sulphenamida (NCBSA) [20] and etilentiouree (ETU) [21] on the corrosion of carbon-steel in diluted ammonia /ammonium solutions at room temperature were studied. The CEMS spectrum of a corroded sample in a solution with 10^{-3} HN_3 concentration with 250 pap NCBSA inhibitor is presented in figure 5. The similar spectra are obtained for MBT and ETU inhibitors. In these spectra there is no evidence for any iron corrosion product at the surface.

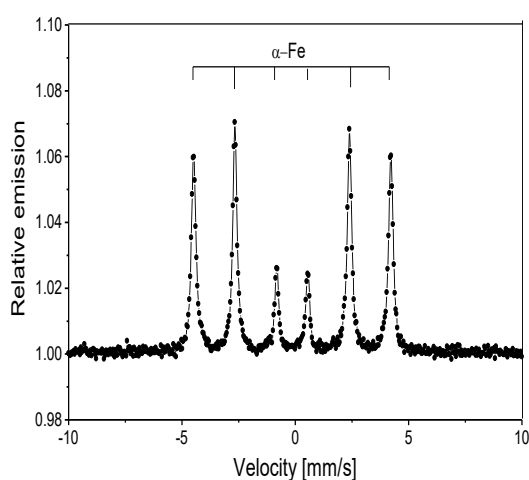


Fig. 5. CEMS spectrum of a corroded sample in a solution with 10^{-3} HN_3 concentration with NCBSA inhibitor
(● data; — fit; --- α -Fe)

In the spectrum there is no evidence for any iron corrosion product at the surface. A relative decrease of the α -Fe line intensities as compared with the sextet obtained in the corrosion process without inhibitor indicated formation of a superficial layer. Also the increased magnetic anisotropy of the CEMS spectra in the presence of the inhibitors confirms the action of the inhibitor. Mössbauer spectroscopy proved together other methods the inhibition action by a formation of a superficial film without iron compounds on the surface of the corroded samples. This layer is interpreted in terms of the formation of complexes between inhibitors and the metal cations present in the carbon-steel structure. The data indicate a good absorbability of inhibitor on the metal surface.

3.3 Corrosion in dilute HCl solutions

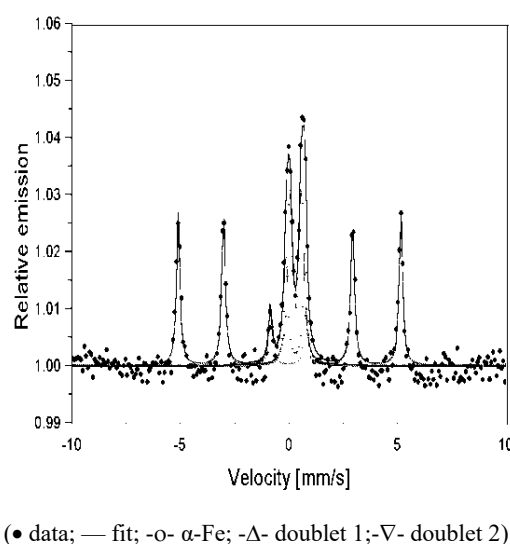
Acid solutions are widely used in industry, the most important fields of application being acid pickling, industrial cleaning, acid decaling, oil-well acid in oil recovery and the petrochemical processes. One of the most aggressive media for the ferric

materials is the aqueous solution of hydrochloric acid. To understand and to reduce the corrosive attack on metallic materials is an important task from economical point of view.

The samples were immersed in a closed system for 3h in solutions of 1 M HCl [22] or 2 M HCl [23], [24]. The CEMS spectrum of the sample corroded in 1 M HCl solution is shown in figure 6. The best fit of the CEMS spectrum uses addition of two Fe^{3+} paramagnetic doublets to the sextet. The parameters of the doublets show the presence of Fe^{3+} and are similar to those shown by nonstoichiometric Fe^{3+} oxyhydroxides. The superficial layer consists of a mixture of α , β and γ - FeOOH . The superficial layer is thicker for sample corroded in HCl solutions then those corroded in ammonia media. In the 2 M HCl solution the corrosion layer is thicker than the layer formed in the corrosion in 1 M HCl solution and with the same superficial compounds.

The importance of inhibition is much greater in solutions of hydrochloric acid since iron and its alloys are the most exposed materials both in industrial and other media. The inhibition effect of five organic compounds for samples corroded in solutions of HCl solutions were investigated: ammonium polymolybdate (APM) [22], figure 7, n-acetyl p-aminobenzene sulfonamide (APAS) [23] N-(2hydroxybenzilidene) thiosemicarbazide (HBTC) [24], Bis (benzothiazolyl) disulphide (BTD) [25] and 2-(cyclohexylaminomercapto) benzothiazole (CMB) [26]. All tested inhibitors operate in the same manner. The process of corrosion is considerable slowed in the inhibitor presence and a superficial compound of Fe^{3+} without a magnetic arrangement is formed. The diminution of the corrosion process is indicates by the increased magnetic anisotropy of the CEMS spectra in the presence of the inhibitors. This means that the depth of the corroded surface layer is lower in the inhibitor presence or corrosion velocity diminished.

Fig. 6. CEMS spectrum of a corroded sample in a 1 HCl solution



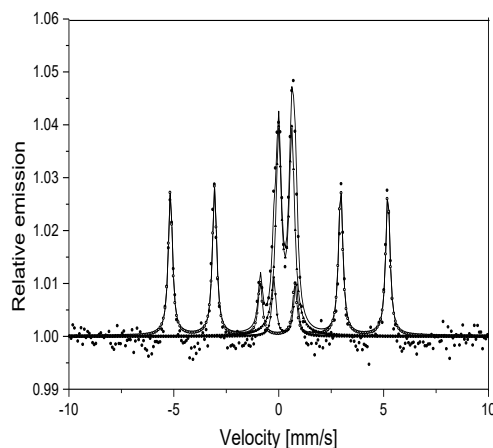


Fig. 7. CEMS spectrum of a corroded sample in a 1M HCl solution with APM inhibitor
(• data; — fit; -o- α -Fe; - Δ - doublet 1; - ∇ - doublet 2)

By estimating the relative area of the superficial compound and the increased magnetic anisotropy of the CEMS spectra in the presence of the inhibitors, results that the compound has a smaller thickness or, in extreme case is similar with the layer formed in the corrosion process without inhibitor. The Mössbauer parameters of the compound in this case do not differ too large from the ones found for the corroded sample in the solution without inhibitor. The new parameters can be ascribed to nonstoichiometric compounds as well as to low crystallinity, *e.g.* ferrihydrites. It is known that ferrihydrite is a precursor of other ordered iron oxyhydroxides. We consider that the organic inhibitors used in HCl solutions act as an incipient “rust transformer” and favours the formation of a “superficial closed layer”. These inhibitors transform some constituents of rust into corrosion inhibiting oxide phases. For the corroded samples in a solution of 2M HCl, the inhibition process is the same as in 1M HCl solutions.

3.4 Corrosion in artificial physiological environments

The studies have been made in order to determine the corrosion reactions, which are necessary for foreseeing the behavior of the materials used in implantology in different conditions, in our case 316L stainless steel, a large used material. These studies were realized by Mössbauer spectroscopy, electrochemical methods and scanning electron microscopy.

The passivation behavior of orthopedic implant was studied as a function of type of physiological media: glucydic, proteic and lipidic. Thus the electrochemical behavior of steel was studied in three artificial media: aminosteryl, intralipid and kabiven [27]. A standard electrochemical cell with a cylindrical working electrode made of 316L stainless steel has been used to study the effect of artificial media. The best fitting of the spectra show the presence of a single line, typically for

stainless steel, which is paramagnetic at room temperature. Mössbauer spectrometry confirms and endures the uniformity, compactness and stability of superficial passive film with the possible exception of some iron vicinities where the superficial layer was affected thus showing the presence of pits. The parameters of the lines are the same, within experimental errors, as for a reference sample. This proves the corrosion resistance of used stainless steel in the tested conditions. In other study the behavior of 316L stainless steel in physiological serum was discussed [28]. A standard electrochemical cell with a cylindrical working electrode made of 316L stainless steel has been used to study the effect of the serum. Transmission [TMS] and electron conversion spectroscopy [CMS] spectra were performed on uncorroded test sample and on sample corroded in a serum solution. All spectra (TMS and CMS) show a central broad line, typical for austenitic stainless steels. We used for them 3 variants for data fit of CMS spectra: single line, doublet and two lines. The best fitting of the spectra was obtained for single line. The parameters of this line of the CMS spectra are the same within experimental errors excepting the effect. This means that the surface was, practically, insignificantly changed during the corrosion process. Mössbauer measurements do not point out micro-structural changes in the investigated samples. The effect decreased slowly for sample corroded in serum. This proved the presence of the thin superficial layer on corroded sample. The Mössbauer spectroscopy proved, thus, the uniformity, compactness and stability of the surface passive films.

We studied the surface situation of 316L stainless steel sample implanted in a femur for 1 year [29]. The TMS and CMS spectra were obtained for uncorroded sample and implanted sample. All spectra (TMS and CMS) show a central broad line, typical for austenitic stainless steels. We used for them 3 variants for data fit of CMS spectra: single line, doublet and two lines. The best fitting of reference sample spectrum was obtained for a single line. For the sample implanted spectrum the goodness of the fit impose two line variant. The relative areas of the two lines were: 27% and 73%. It was clear that during implantation a change in the superficial microstructure took place and a corrosion process was presently. Another difference between the reference sample and implanted sample consisted in a decrease of the intensity line for implanted sample. This proved the presence of thin superficial layer on implanted sample. We believed, inspired by references, that surface layer consisted mainly of oxide species. A slight improvement of goodness of the fit, within experimental errors, was obtained for implanted sample by using a sextet line near two lines. This fact suggests a possible apparition, in a small proportion of a martensitic phase on surface.

4. Conclusions

The studies carried out show that Mössbauer Spectroscopy is a very effective method in the study of corrosion phenomena, especially in the case of ferrous

materials. For a better understanding of corrosion, a correlation of the Mössbauer results with those obtained by other methods is useful and necessary.

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