Measuring Hydrogen Gas Loading Using NMR Spectroscopy

TECHNICAL AREA:

This disclosure describes a design of a micro NMR device, and the method of monitoring its signals including free induction decay (FID), and relaxation time (T_1 or T_2), to achieve in-situ system calibration in hydrogen/deuterium gas reactions with solids materials.

BACKGROUND:

Nuclear Magnetic Resonance (NMR) is based on the fact that when a population of magnetic nuclei is placed in an external magnetic field, the nuclei become aligned in a predictable and finite number of orientations. It is a nondestructive evaluation technique useful for characterizing organic matrix composites and other polymer based materials. NMR depends on the interaction between the nuclear magnetic moment and a magnetic field and thus it is sensitive to localized field variations caused by molecular motions, changes in molecular or crystal structure, and chemical composition differences.

A common application of NMR to material science involves measurement of the hydrogen nucleus (proton) NMR signal. The proton NMR signal is very strong and easily measured. Much of the physical and chemical information available through the use of NMR is associated with the relaxation characteristics of the nuclear magnetic moments, which can be measured using pulsed NMR techniques. The energy exchange between nuclear moments and the surrounding lattice is characterized by the spin-lattice relaxation time, T_1, while the energy exchange among nuclear magnetic moments is described by the spin-spin relaxation time, T_2. These relaxation times are very sensitive to molecular motions and structural changes and can be used to provide both qualitative and quantitative information on the dynamic environment in which the nuclei are located. Proton NMR has been used to characterize water absorption,

molecular diffusion, environmental degradation, aging, degree of cure, and modulus variations.

EXISTING TECHNOLOGIES:

NMR Relaxation technique is widely used as a diagnostic method in biology, medical, material science, engineering aspects. Researches also use proton NMR to study metal-hydrogen (e.g. n-Pd-$H_{0.7}$) nanoparticles.[4-5] However, no one has use this technique in calibrating reactors involving hydrogen gas.

PROBLEMS WITH EXISTING TECHNOLOGIES:

In-situ system calibration is a critical and relatively unexplored field in reactions involving hydrogen gas and metal lattice interactions. For example, it is difficult to monitor the hydrogen/deuterium loading status in metals lattices (e.g., the amount of hydrogen absorbed in Pd metal). Traditionally, people monitor the system resistance, the hydrogen gas pressure/volume to determine the loading ratio. These methods are susceptible of side reactions, change of outer conditions etc. and have limited accuracy. Also, it remains challenging to probe chemical environment, the interactions between metal lattice and hydrogen/deuterium atoms. These factors are important to understand and monitor for any operating hydrogen reactors.

SUMMARY OF THE PROPOSED SOLUTION AND THE ADVANTAGES THE PROPOSED SOLUTION PROVIDES:

This disclosure describes an in-situ system calibration method using NMR technique by monitoring the hydrogen/deuterium relaxation time, free induction decay (FID), T_1 and/or T_2 in nuclear magnetic resonance. T_1 and T_2 are extremely sensitive to dynamics of the molecular mobility in the hydrogen environment. So the free hydrogen and lattice hydrogen have different relaxation time. Therefore, this technique can efficiently and accurately monitor the interactions between hydrogen and metal lattices, and recognize the ideal

loading status. With a predetermined calibration parameters, we can obtain in-situ system calibration and diagnosis for reactors.

DETAILED DESCRIPTIONS OF THE PROPOSED SOLUTION AND FIGURES:

The NMR diagnostic system adopts the conventional NMR configuration, includes a coil closely surrounding the reactor, and a magnet creating a uniform magnetic field perpendicular to the applied radio frequency (RF) pulse. These two embodiments described below use exothermic reactors as examples. Those exothermic reactors use metal hydride as reactants and the hydrogen loading ratio achieved by the metal hydride is an important indication of the reactor's efficacy. An in-situ hydrogen loading measurement device using NMR techniques becomes a handy calibration tool of the exothermic reactors.

The coil is a RF pulse generator as well as a signal detector. The RF pulse is usually in MHz range, and the relationship between a nucleus' frequency v and magnetic field strength of the permanent magnet is given by Equation 1. The RF pulses used here are 21 and 53 MHz for H-Pd system.[4]

$$(v = (-\gamma B_0)Hz/2\pi) \quad \text{Eq. 1}$$

In this equation, Hz is the RF frequency, γ is the gyromagnetic ratio (26.7522128×10^7 rad T^{-1} s^{-1} for proton), and B_0 is the magnetic field strength of the magnet expressed in Tesla.

Under the magnetic field, the applied RF pulse excites the hydrogen/deuterium nuclei, and then relax during the signal acquisition time, giving an NMR signal due to an oscillating voltage induced by the precession of the nuclear spin in the X-Y plane. This results in the observed exponentially decaying sine wave, as shown in Figure 4 a and b. This decaying sine wave is termed free induction decay (FID). The induced current then go through the

current amplifier and an analog digital converter, and become digital current signals (NMR signal) being detected.

The direction of the magnet does not have to be perfectly perpendicular to the RF pulse, however, the device is optimized when the magnetic field and RF pulse are perpendicular. The magnet can be permanent magnet or magnetic coil, as long as there are sufficient uniform magnetic field inside the magnet that can cover the coil. Permanent magnet are used as illustration in the device diagram in Figure 1 and Figure 2. The diagnostic system (the coil) can cover the entire or partial of the reactor.

The micro NMR device, shaped like a donut with the reactor sitting in the middle, as shown in Figure 3, should have smooth inner surface and can be attached and detached to the reactor easily.

Highly conductive metal piece can produce inductive current under alternating electromagnetic field, and disturb NMR signals, so if the NMR device is outside the reactor, the reactor cannot be made of metal, as shown in Figure 1a. Ceramic and quartz are good choice of reactor material.

If the coil is inside of the reactor, there is no restriction in reactor materials. The device configuration is illustrated in Figure 1b. The reactor surface can also be made of the permanent magnet itself, with the coil attached to the inside of the magnet. Also, the device is not suitable to test bulk metal piece (metal rod etc.), but can be used to analysis metal thin films, metal nanoparticles, metal oxides, metal hydrides, gases, solutions etc.

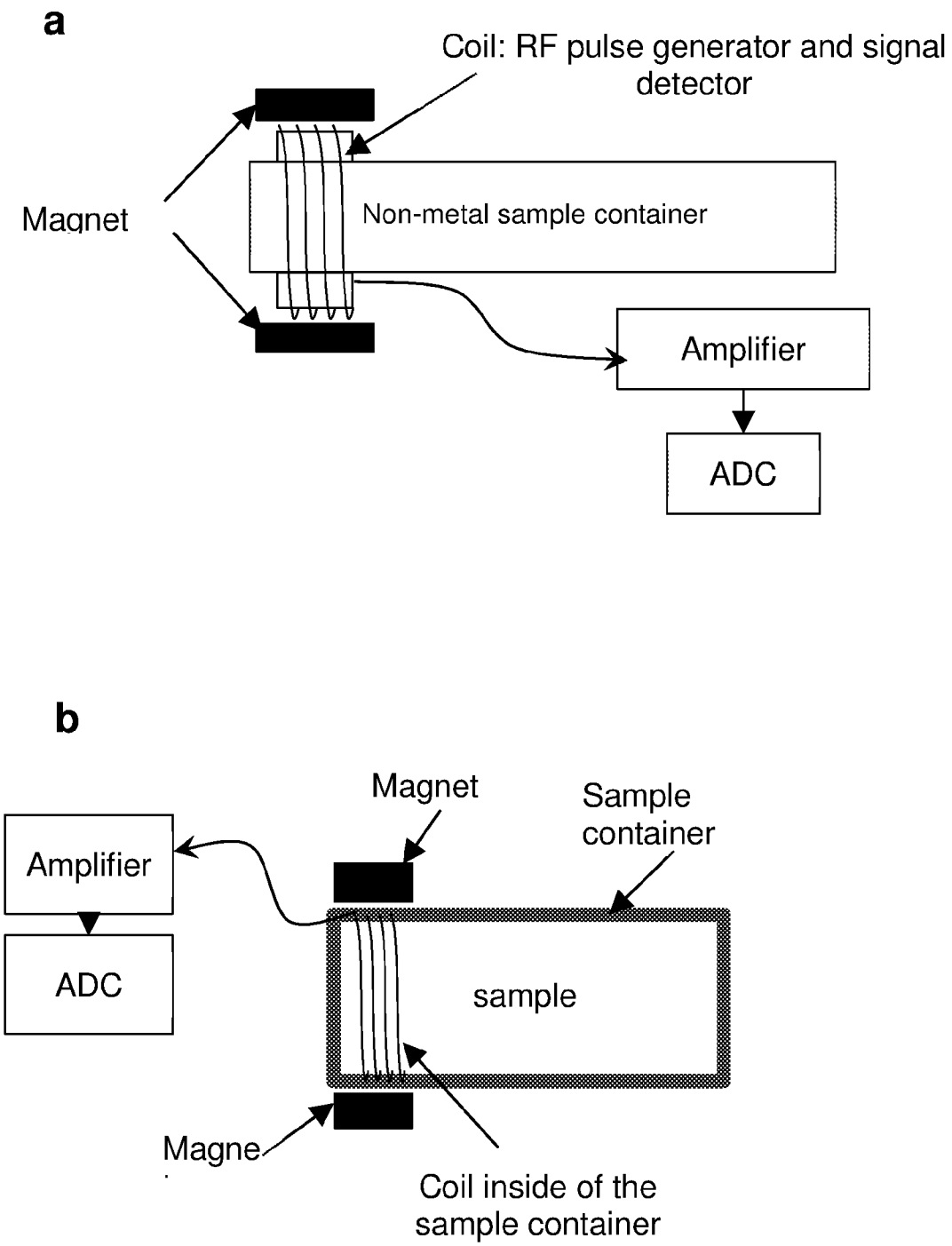


Figure 1. a). The diagram of the detachable NMR calibration system. b). The diagram of the build-in NMR calibration system with the coil inside of the reactor.

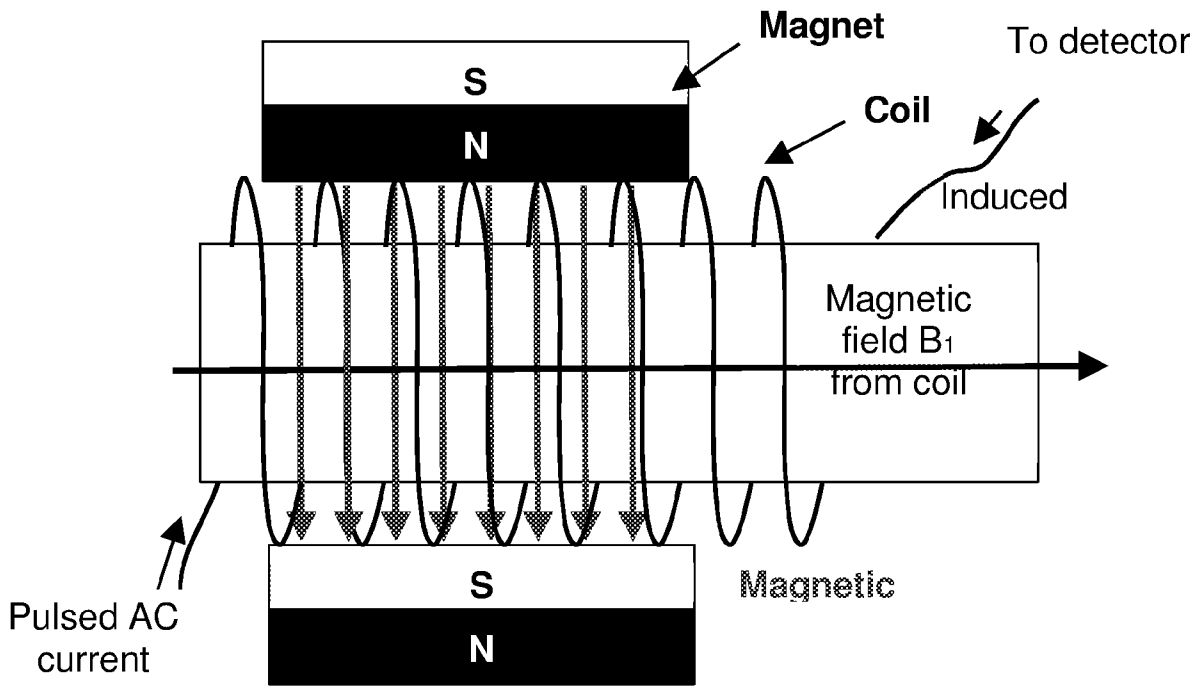


Figure 2. The detailed design of calibration system.

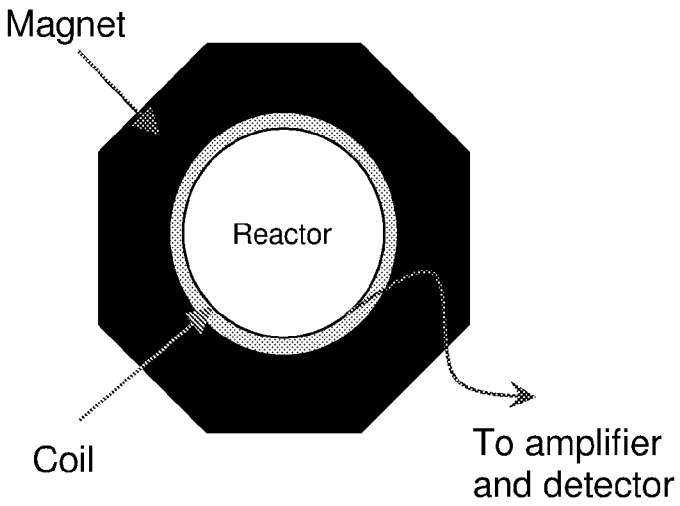


Figure 3. The side view of the calibration device.

Based on the chemical environment of hydrogen (free hydrogen atoms or photons, in the lattice), concentration and the distance between each hydrogen nuclei, each stage (initializing, triggering, and operating) has its own characterization FID, T_1 and T_2 signals. A calibration database will be generated by collecting data for the initial system before any activation, fully operating systems, and deactivated systems. The NMR measurement will be performed during the entire process, and T_1 and T_2 would be derived from the FID signals that collected by the coil and received by the amplifier and ADC. The data acquisition starts before any activation of the system, and kept collecting data during the activation process, normal operation, until the reactor has been shut down and achieve stable status.

During the calibration, the applied voltage intensity and frequency in the coil will be tuned and accurately monitored by the ADC at the beginning of each step (before activation, during activation, after activation, and termination) and kept constant.

During the calibration, a calibration plot will be generated with four parameters (FID intensity, duration, derived T_1 and T_2) vs reaction time, with the key event labeled (initialize, activation, reacting and termination).

During the calibration, the signals of an empty reactor (container) will be collected under the same parameters, and be used as a background signal.

The system can be diagnosed based on the characteristic FID, and/or T_1 and/or T_2 on each reaction stage. The calibration methodology is described in the procedures.

Once the calibration database was established, the device can be applied to the in-situ system diagnose by performing NMR technique and monitoring FID, T_1 and T_2.

Procedures:

1. Generate a calibration database

There are three reaction stages in an entire process: initial stage (before any reaction starts), operation stage (including the initial activation and operation stages), and the termination (including reactor shutting down and returning to the original stable status). The calibration process will be performed over the entire process.

i. Under the constant magnetic field (B), apply a radio frequency (f) pulse produced by the coil, and record the FID signal from the induced current in the coil by the current amplifier and the analogue digital converter.

ii. There are three reaction stages: initial stage (before any reaction starts), operation stage (including the initial activation and operation stages), and the termination (including reactor shutting down and returning to the original stable status), Start data collection before any reaction started, and stop until the reactor has been shut down and returned to stable status.

iii. One calibration plot over three stages will be obtained. The parameter (the current and RF pulse frequency in the coil) are adjusted to achieve the best signal intensity at the beginning in each stage.

Iv. For each stage, signal will be collected with an empty reactor/container and be used as a background.

2. Data processing

FID: Under the magnetic field and the RF pulse perpendicular to it, the induced current go through the amplifier and analogue digital convertor, and its intensity and decay time was recorded and analyzed. The signal intensity and decay time is related to the hydrogen chemical environment and concentration.

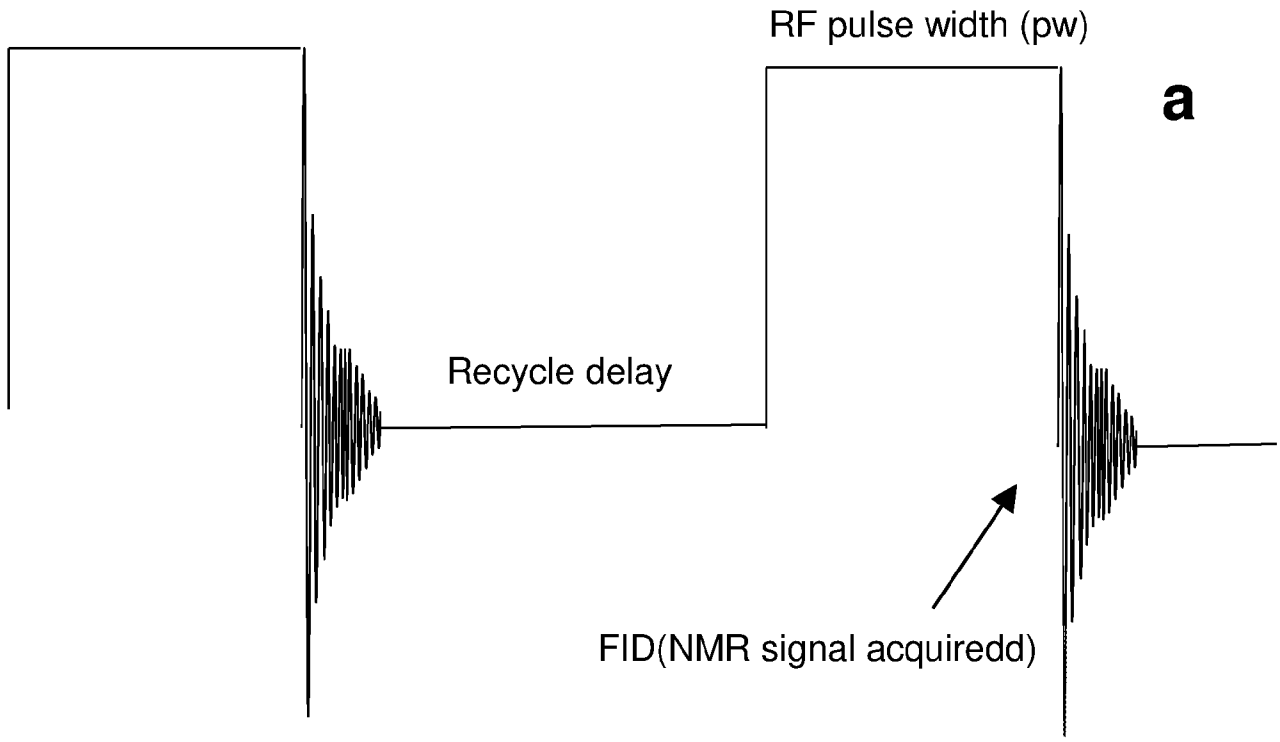
T_1 and T_2 was monitored by a conventional NMR technique, which are obtained by the exponential fitting of different RF pulse frequency vs magnetization intensity.

Conventionally, T_1 was measured by applying a pulsed current with sine wave shape, and monitor the inductive signal intensity. In our design, the pulsed current will be changed into a square wave etc. and perform the same procedure to calculate T_1.

3. System diagnose

During the reaction operation, same current pulse was applied with calibration procedure, and record the raw spectra (FID spectra), and derive T_1 and T_2 through exponential fitting, by comparing and diagnose the system, as shown from Figure 4 and 5. A significant decrease of FID relaxation time, as well as T_1 and T_2 are expected when hydrogen are loaded into the lattice, as shown in Figure 6-8.

By comparing the ratio of T_1/T_2, we can also get the relationship of the hydrogen loading in the lattice and the T_1/T_2 ratio, as shown in Figure 9.[3] In addition, study indicates the T_1 relaxation rate (R_1) of hydrogen in the nanocrystalline particles is significantly greater than hydrogen in coarse-grained system. e.g. At 155 K the measured R_1 for $PdH_{0.7}$ (at 21 MHz) is 33 s^{-1}, as compared with 4.6 s^{-1} for hydrogen in the coarse-grained system. So the device can be used to analysis particle size.[4] In a single stage (e.g. operation stage), measuring T_1/R_1 can indicate particle size.


RF pulse width (pw)
a
Recycle delay
FID(NMR signal acquiredd)

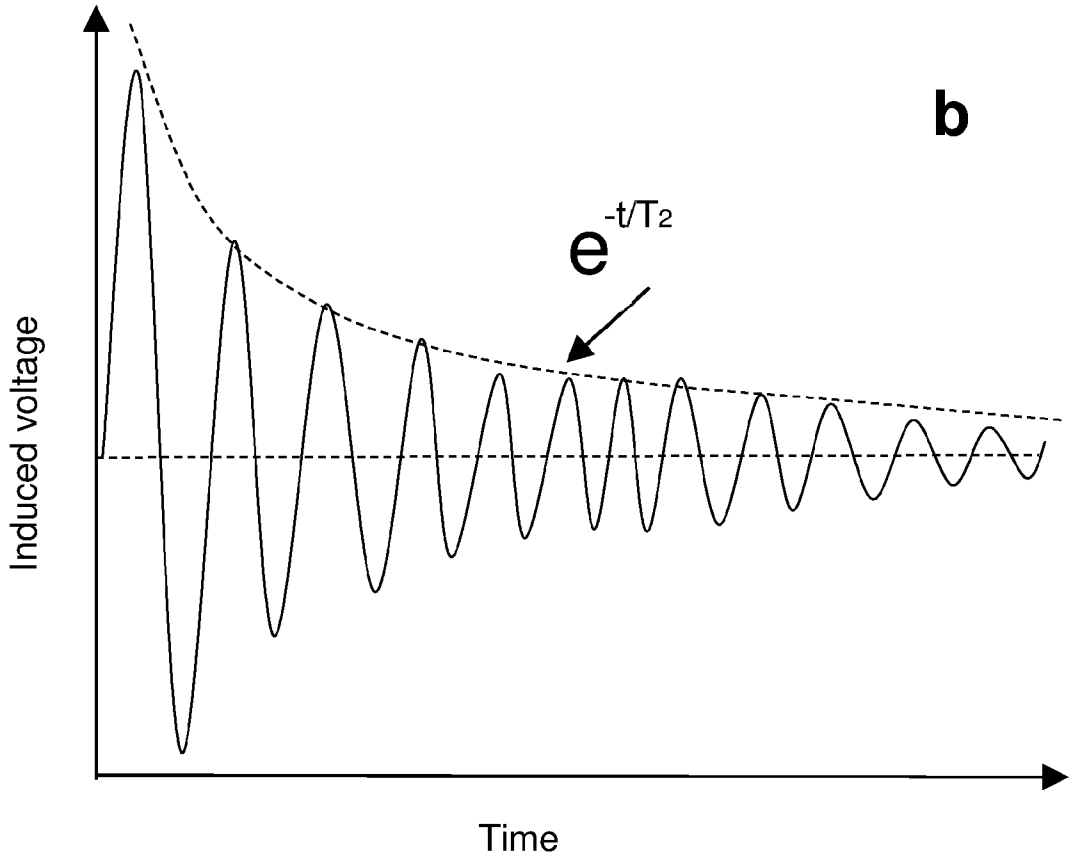


Figure 4. Schematic representation of a) NMR raw spectra and b) free induction decay signals, plotted as induced voltage vs signal relaxation time, and its exponential fitting.

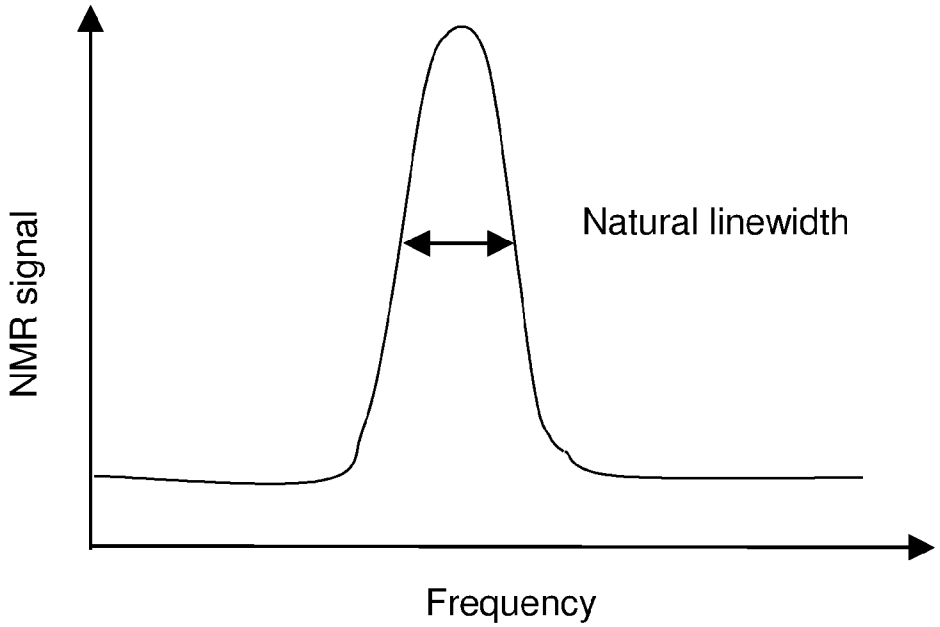


Figure 5. NMR spectra from the Fourier Transform of FID, plotted as intensity vs frequency.

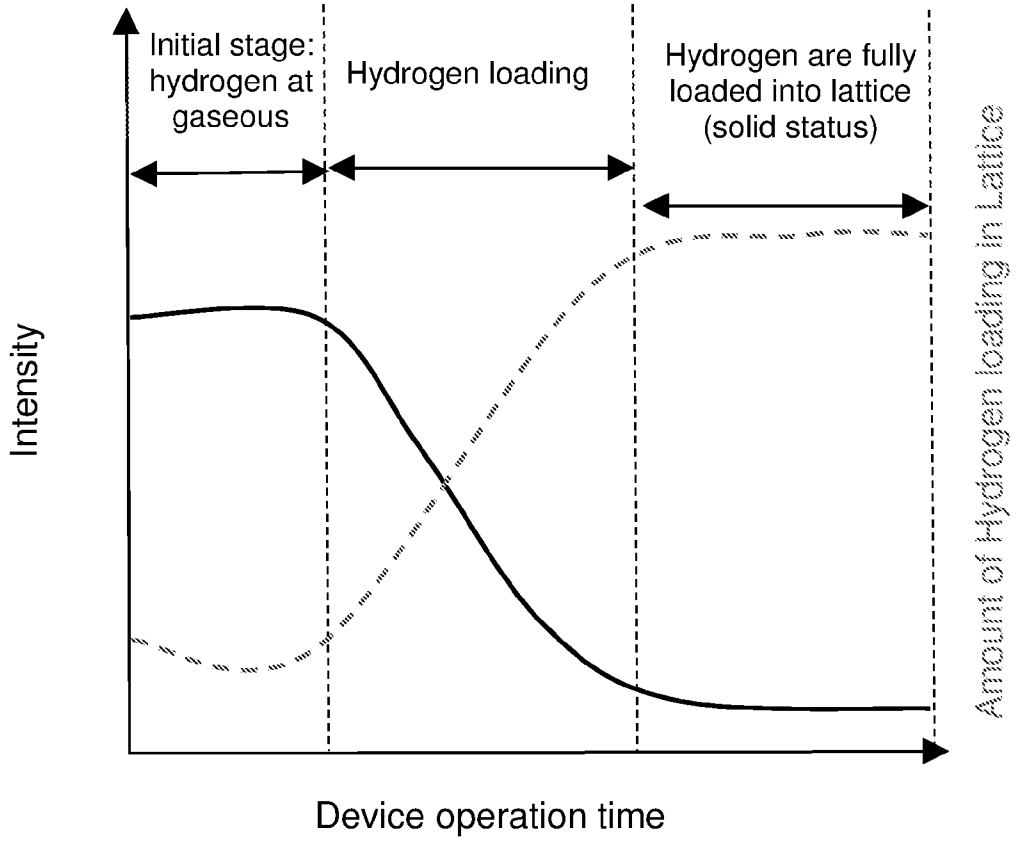


Figure 6. Proposed relationship between FID relaxation time and the amount of hydrogen loading into material's

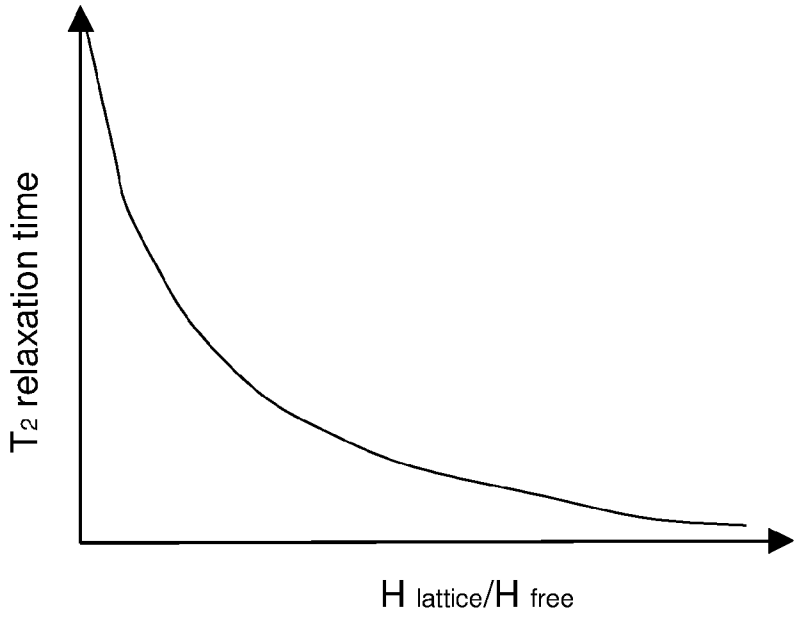


Figure 7. Proposed relationship between T_2 and the hydrogen loading into material's lattice.

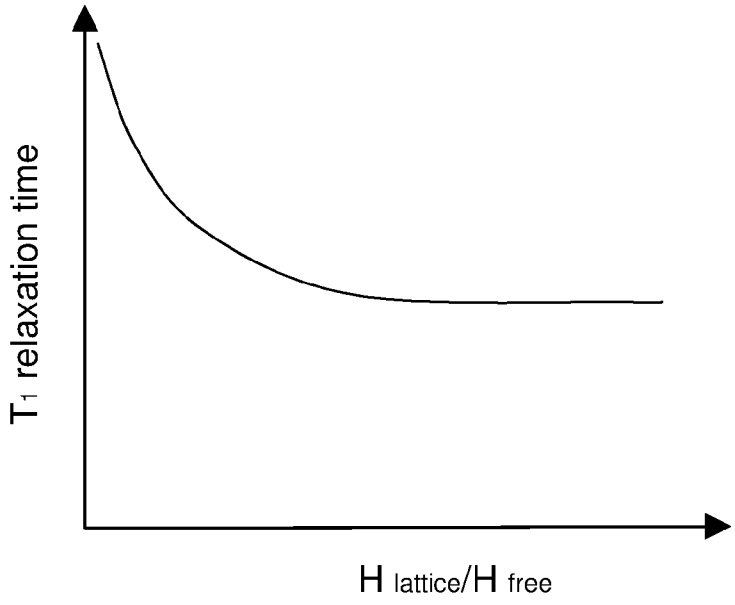


Figure 8. Proposed relationship between T_1 and the hydrogen loading into material's lattice.

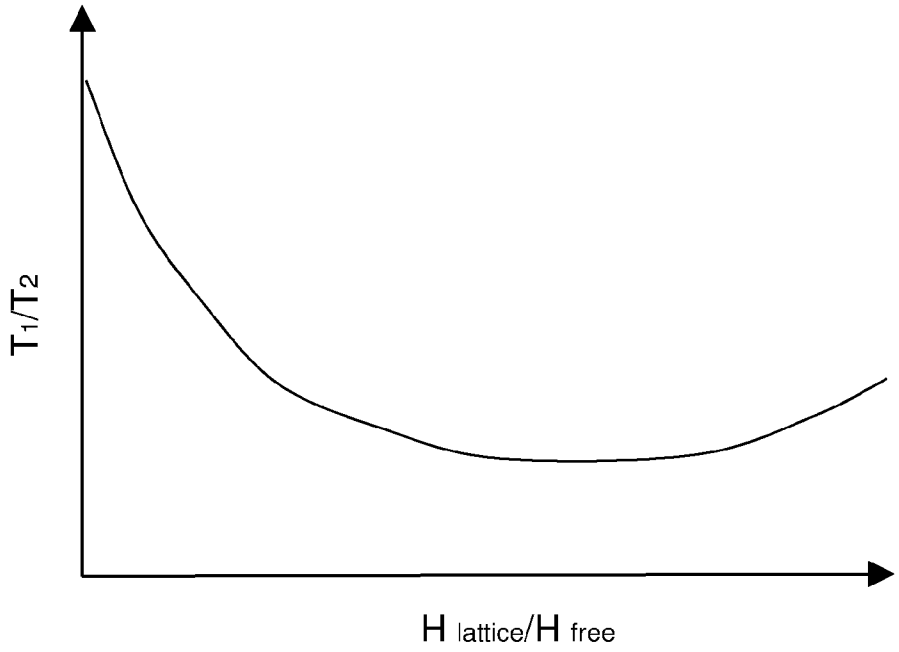


Figure 9. Proposed relationship between T_1 /T_2 ratios and the hydrogen loading into material's lattice.

REFERENCES:

1. G. A. Matzkanin. A Review of Nondestructive Characterization of Composites Using NMR. *Proceedings of the 3rd International Symposium Saarbrücken, FRG*, **1988**, 655-669.

2. H. W. Reinhardt. Characterization of Fresh and Early Age Concrete Using NDT. *Proceedings of the 3rd International Symposium Saarbrücken, FRG*, **1988**, 407-421.

3. W. N. Hardy. Nuclear Spin Relaxation in Gaseous H_2 at Low Densities. *Canadian Journal of Physics*, **1966**, 44, 265-280.

4. J. W. Hanneken et. al. NMR Study of the Nanocrystalline Palladium–hydrogen System. *Journal of Alloys and Compounds* **2002,** 330, 714–717.

5. D. S. Sibirtsev et al. Hydrogen in nanocrystalline Pd: a nuclear magnetic resonance study. *Solid state communications,* **1998**, 108m: 583-586.