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Masterarbeit

Drying shrinkage and cracking in cement-based materials: non-destructive detection by single mode resonant ultrasound spectroscopies

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Formulation of the master thesis

Drying shrinkage and cracking in cement-based materials: non-destructive detection by single mode resonant ultrasound spectroscopies

Concrete and cement-based materials in general have been shown to share with rocks, poly-crystalline metals, consolidated, e.g., sintered ceramics and unconsolidated granular materials, e.g., soils and micro-cracked materials at large, even when single crystalline, a specific nonlinear elastic behavior phenomenology which has been called "non-classical" or mesoscopic nonlinear elasticity (NME). NME needs to be compared with the "classical" nonlinear elasticity of any material, exemplified by a nonlinear stress-strain constitutive equation when the strain amplitude is finite ($\geq 10^{-7}$) instead of infinitesimal ($10^{-10} \div 10^{-7}$) and stemming from anharmonicity of vibrations at the scale of atomic lattices in crystalline phases and in the presence of finite strain amplitudes. NME does not stem at the atomic scale, rather from a series of structural features and phenomena involving them which typically exist and occur at larger length scales than the atomic lattice ones: shear deformations at grain boundaries in poly-crystalline materials, interaction of dislocations in single- and poly-crystalline materials, clapping of the two sides of rough interfaces subjected to dynamic deformations, where the interface may be an autogeneous feature, e.g., in a composite layered material, or it may be damage artifacts as micro-cracks, and debonding of interfaces in layered composites.

Stemming from such types of features and processes, measurements of NME, typically of nonlinear mesoscopic quasi-static and dynamic elastic moduli and of nonlinear wave amplitude attenuation, have been shown to have unparalleled sensitivity to the presence and to the temporal evolution of such features and processes, starting from their early development, making them ideal non-destructive evaluation (NDE) methods, based on elastic (seismic, sound, ultrasound,) waves, for detecting and characterizing damage.

Measurements of NME have been frequently grouped under the umbrella name of Nonlinear Elastic Wave Spectroscopy (NEWS). Applications of NEWS for damage detection and characterization in cement-based materials have so far spanned the following cases: the sensitive detection of drying shrinkage-related cracking, the assessment of the degree of alkali-silica reactivity of aggregates, the detection and characterization of micro-cracking induced by sulfate attack or by freeze thaw cycles or by delayed ettringite formation.

Extensive work has been already published showing the superiority of NEWS methods, compared with standard NDE ones based on linear ultrasounds (measurements of linear Young modulus and wave amplitude attenuation), in terms of sensitivity to early development of damage, frequently in the form of micro-cracking. A very small number of studies have addressed the detailed understanding of the case-by-case physical sources of NME, especially for cement-based materials.

Among the physical sources of NME, few and contradicting results have been published regarding the role of the water saturation degree in determining the features and the "degree" of NME.

Goals

• Systematically investigate the evolution of nonlinear mesoscopic elastic moduli of cement-based materials during drying shrinkage, uncoupling the effects of shrinkage-driven micro-cracking from the pore

space saturation.

- Perform the investigation in the presence of different environmental relative humidities (43% and 75%), thus with different drying drives.
- Realize an experimental setup for performing the investigation under very well controlled environmental conditions, in terms of relative humidity and temperature, for the NEWS measurements.

Brief overview of how to achieve the goals and work plan:

- An experimental drying shrinkage campaign will be setup during which both linear shrinkage and single mode nonlinear resonant ultrasound spectroscopy (SIMONRUS) measurements will be performed at different stages.
- The campaign will involve both cement-based materials (mortars) and other building or geo-materials (a type of sandstone), in order to compare between porous materials with large predisposition to drying shrinkage (the cement-based ones) and others with less (certain types of stones of interest as building materials).
- Special focus will be put on performing the linear shrinkage and time-lapsed SIMONRUS measurements under controlled environmental conditions in terms of temperature and relative humidity, installing the currently available SIMONRUS setup within a glove box, able to control temperature and relative humidity in order to achieve similar values as those of the dessicator(s) used for the drying. The implementation of the glove box will be integral part of the experimental work. The rationale for such high level of boundary conditions controls is to reduce as much as possible spurious sources of microstructural changes in the specimens, e.g., re-saturation, while at the same time allowing to perform the SIMONRUS measurements with a high degree of accuracy and collecting sufficient statistics, both of which require multiple and prolonged repetitions on a time scale of tens of minutes, a time period long enough to perturb the drying process.
- In order to try to assess whether the only coupling between saturation degree and the NME behavior derives from shrinkage and respective cracking at low saturation levels, for each mix design type, two versions will be realized, one without the use of shrinkage reducing admixtures (SRA), the other with. The goal is to achieve, for each mix design, minimum difference in evaporative drying kinetics and dynamics while obtaining significant differences in shrinkage, thus in micro-cracking. Previously published experimental results hint at the possibility of achieving very similar drying while still having, in the absence and in the presence of SRA, very different levels of shrinkage.

Eidesstaatliche Erklärung

Hiermit erkläre ich, die vorliegende Arbeit selbstständig und ohne fremde Hilfe verfasst und keine weiteren als die angegebenen Quellen und Hilfsmittel verwendet zu haben.

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Ort, Datum, Unterschrift

Abstract

Cement-based materials are extraordinary sensitive to cracking evoked by drying. By detecting the elastic behaviour via NEWS methods, the progress of internal damages and microcracks can be observed and evaluated. Due to the drying shrinkage, this work deals with the question, how water saturation degree influences the elastic behaviour of mortar and Vosges sandstone in non- and equilibrium, comparing the similarities and differences, whether the water saturation degree is coupled with the occuring microcracking and furthermore, how Shrinkage Reducing Admixture (SRA) effects the linear and nonlinear elastic behaviour of mortar. For examination, single mode linear and nonlinear resonant ultrasound spectroscopy (SIMORUS/ SIMONRUS) is applied to multiple specimens at different drying ages, supported by classical mechanical methods to determine additionally the shrinkage, drying rate and internal relative humidity value. Thereby, the Vosges sandstone shows a different development in nonlinear elastic behaviour than in previous publications [VCJZ02] and [JS05] by varying monotonically in decreasing nonlinearity strength with decreasing internal relative humidity value. In contrast, the mortars are stronger influenced in nonlinear behaviour by the damages and stresses caused by drying shrinkage than the water saturation itself, whereby the SRA reduces the nonlinearity strength by decreasing the shrinkage of the specimens.

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List of acronyms

CRP Constant Rate Period
EoS equation of state
FRP Falling Rate Period
NME mesoscopic nonlinear elasticity
NDE non-destructive evaluation
NEWS Nonlinear Elastic Wave Spectroscopy
RH relative humidity
RUS Resonant Ultrasound Spectroscopy
SIMORUS Single Mode Linear Resonant Ultrasound Spectroscopy
SIMONRUS Single Mode Nonlinear Resonant Ultrasound Spectroscopy
SRA Shrinkage Reducing Admixture

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1 Introduction

By improving knowledge of building materials and new discoveries, the need for new non-destructive methods raised successively. Hence, ultrasound velocity-based measurements were first adopted in the 1940s, where the theory of elasticity was utilised to obtain resonance frequency measurements. In the 1960s, the first Resonant Ultrasound Spectroscopy (RUS) measurements were performed on crystalline materials by Frasier and LeCraw. By help of the upcoming support of computers, the method was further developed and mainly applied to geo-materials. [May96]

Due to the similiarity in properties of rocks and cement-based materials, RUS was used for the characterisation of cementitious materials as well, whereby the interpretation of results is more complex based on the differing elastic behaviour. Nevertheless, the sensitivity of the method to internal damages and microcracks is outstanding and therefore promising for observation and detection of durability questions in cement-based materials, (mostly vor SIMONRUS).

So far, multiple new insights into rocks have been published in the field of NEWS, but comparably few in regard to cementitious solids, particularly for the influence of drying and corresponding changes in water saturation degree. Therefore, this master thesis considers the process of drying in mortars and a type of sandstone.

Moreover, this work focuses on the following question: How does the water saturation degree or, rather, the internal RH influences the elastic behaviours of both materials and which differences are recognisable? Furthermore, how does SRA influences the elastic behaviour during drying shrinkage? Which trends are noticeable? How significant are the results, when the system is still not in equilibrium compared to those in equilibrium? Is the evolution of the measured nonlinear elastic behaviour solely related with the cracking due to drying shrinkage or is it also coupled to the saturation degree decrease itself, independently from the resulting degree of cracking? Is it possible to perform an uncoupling to get only the effects of cracking on the measured nonlinear elastic moduli?

These questions are examined by successively characterising, during drying, the specimens by SIMORUS and SIMONRUS measurements as well as other measurement of drying and shrinkage parameters. The Vosges sandstone was dried at six different RH values along the desorption branch of a sorption isotherm. In regard to the velocity of drying of mortars, two different mortars (one with SRA, one without SRA) were dried at two RH values (43%RH and 75%RH). The results have been critically evaluated in the framework of the theory of elasticity (linear/nonlinear and classical/non-classical).

At first, a theortical base is built by explaining the corresponding equations of wave propagation in solids (Ch. 2.1), the theory of elasticity applied to rocks and cement-based materials (Ch. 2.2) and drying shrinkage in the cementitious solids (Ch. 2.3). As presentation of the used methods and machines, Chapter 3 describes the used experimental setups. The results of the measurements and their discussion is divided into four sections in Chapter 4 where the Vosges sandstone, the mortars with SRA and without SRA are considered and, afterwards, compared with each other. Various parameters, like linear and nonlinear single mode RUS measurements and quasi-static mechanical as well as drying parameters, are included in the analysis and evaluation as well (Ch. 4). To summarize this thesis, the conclusions are presented in Chapter 5, where an outlook is also provided.

2 Theoretical bases

2.1 Basics of linear elastic wave propagation in solid materials

2.1.1 Longitudinal and shear waves in 3D bulk (unbounded) media

Depending on the direction of the elastic wave oscillation compared with the direction of the wave propagation, a wave is called transverse or longitudinal. If the displacement direction is parallel to the propagation direction, it will be a longitudinal wave. In case of a transverse oscillation, i.e., an oscillation occurring along a direction orthogonal to the propagation direction, it will be a transverse, also called shear, wave. [PR15, p.98] [Gra91]

The size of the specimen is a decisive parameter for the velocity of a longitudinal wave in finite solids. Here, the wave equation is contextualised for the analysis of longitudinal waves considering a finite cross section with linear size much smaller than size of specimen along the direction orthogonal to it. This is the assumption mentioned above of a finite specimen very much elongated in one direction compared with the other two mutually orthogonal to it, leading to the 1D approximate formulation of the wave equation. Under this assumption, the Young's modulus (Y) is introduced. It expresses the ratio of the longitudinal stress, along the elongation (X-)axis, in the specimen to its respective longitudinal strain. Though, a longitdunial strain also occurs in Y-axis and Z-axis, whereby σ_{xx} is considered in the approach of 1D thin rod. Hence, the following wave equation results which can be applied for each 3D direction by adding indices of the corresponding direction [PR15, p.149]:

$$\frac{\partial^2 \eta}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 \eta}{\partial t^2}, \text{ with } c^2 = \frac{Y}{\rho}$$
(2.1)

whereby, η represents the displacement component along the X-axis $\eta(x, t)$. c is the longitudinal phase wave velocity.

Shear forces can develop due to the material properties during the generation and propagation of a longitudinal wave. In general isotropic media, couplings exists between longitudinal deformations and shear ones such that a longitudinal wave also creates a lateral distortion of the medium, thus launching also a transverse wave. The strength of such couplings, for an isotropic elastic material, are quantified by the value of the Poisson's ratio σ , defined

$$-\frac{\partial\beta}{\partial y}/\frac{\partial\eta}{\partial x} = \sigma \tag{2.2}$$

The shown terms express different strains caused by the source of a longitudinal wave: The longitudinal strain is described by $\partial \eta / \partial x$ and the strain produced by lateral distortion, is here indicated as $\partial \beta / \partial y$. In this case, β is the displacement in the y direction and it is a function of x and y, just as the X-displacement wavefield is also a function of x and y (in the simplified case of a 2D medium only). The Poisson's ratio can be further expressed in terms of two other material parameters called the Lamé's elastic constants λ and μ : [PR15, p.149 et seq.]

$$\sigma = \frac{\lambda}{2(\lambda + \mu)} \tag{2.3}$$

Both Lamé's constants are always positive. This fact, according to the the definition of Poisson's ratio in Eq. (2.7), leads to ($\sigma < \frac{1}{2}$, commonly $\approx \frac{1}{3}$). The Young's modulus can be expressed as a function of the two Lamé's constants,

$$Y = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu} \tag{2.4}$$

The 2nd Lamé's, also called shear modulus or rigidity modulus, constant μ expresses the transverse rigidity in a bulk solid. This constant is the ratio of the transverse stress to the transverse strain. μ plays the same role for transverse waves in a bulk, 3D specimen or in an infinite medium as the Young's modulus does for longitudinal waves in an elongated specimen, approximately described, propagation-wise, as a 1D medium. Due to the transverse rigidity, μ affects the equation expressing the wave phase velocity of a longitudinal wave in a bulk specimen or infinite medium in the following way:

$$c^2 = \frac{\lambda + 2\mu}{\rho} \tag{2.5}$$

By plugging Eq. (2.8) into Eq. (2.5) for the square of the longitudinal phase velocity in a 1D medium and comparing the results with the expression of such velocity in a 3D bulk specimen, it can be concluded that the velocity of longitudinal waves is higher in a bulk solid than along an elongated 1D specimen. [PR15, p.150 et. seq.]

The physical properties of the propagation of (longitudinal) waves depends on the shape and size of the solid specimen. While in principle it would be needed to consider always the description of elastic wave propagation in a 3D bulk medium, considering all the possible forms of coupling between different strain components, it is possible to significantly simplify the corresponding scalar wave equations and reduce their numbers to be solved to compute the wavefields by considering the shape and aspect ratios of the bound specimen where the propagation occurs (see equations above). [LL70, p.113] Such simplifying, e.g., by the use of the 1D approximation mentioned above, reducing the longitudinal phase wave speed being dependent on the Young's modulus, can be applied within the context of this Master Thesis project because all of the specimens used for the ultrasound measurements were characterised by elongated shape with large enough aspect ratios. Under such conditions, the description of the ultrasound propagation is the same when considering the propagation of an elastic wave in a thin rigid rod, for which the longitudinal wave equation assumes the same form as in Eq. (2.5), with the same expression for the longitudinal phase wave velocity. A longitudinal wave is typically considered to propagate in a thin rod without significant transverse distortion, under the first order of approximation used. While so far the elastic wave propagation has been mainly considered in unbounded media, which, in the rod, i.e., 1D, approximation means an infinte rod, the next step in the elastic wave propagation description consists in taking into account what happens in the used real specimens, which behaves mainly as finite rigid rods with either fixed ends or free ends or any combination of the two types of 1D boundary conditions. When such boundary conditions are taken into account, one deals with patterns of a vibration of the finite rod which are similar to the vibration patterns of strings. [Gra91] [PR15] [BD94]

2.1.2 Longitudinal and shear waves in 1D finite (bounded) media (thin finite rods)

The vibration patterns due to longitudinal or shear waves in thin and finite (bounded rods) can be described by wave equations similar to the ones used to describe the oscillation of an elastic string. E.g., when children try to imitate snakes by swinging one side of a robe while the other side is left free of moving in space. While wave in an elastic string are mainly of shear type, in thin rigid rods they can be both of longitudinal type or of shear type depending upon the type of excitation at one end. Despite the differences in which direction the displacement vector oscillates compared with the direction of the string/rod, what is common from a mathematical description point of view is the consequence of the boundary conditions leading to well defined patterns of spatial distributions along the string/rod of displacement maximum amplitudes, the displacement field oscillating between +/- such amplitude in harmonic way. Such defined patterns of vibration of the string/rod are called standing waves. In regard to the velocities of the two types of waves, it has to be mentioned that the considerations as waves are based on the phase relationship, not their progressive motion, because standing waves, by definition, do not progress in space with a distinctive visible "front" whose advancement can be used for measuring propagation velocity. [PR15, p.95 et. seq.] Nevertheless, the expression of the different velocities is similar to the general one in section 2.1.1. [Gra91] [PR15] [BD94]

The model of shear wave propagation in a string and the corresponding observables and parameters are used here for introducing the basic concepts about 1D standing waves, with the remark that the same concepts are transposable and usable for both shear and longitudinal waves in thin rigid rodes, the latter being better approximated models of the conditions for elastic wave propagation in the investigated specimens. A set of measurable variables and description is provided in what followed for elastic strings, with the possibility of using them immediately for thin rods. The first important parameter is the wave impedance of a string synthesizes in itself two energy storing parameters, inertia and elasticity, if the medium is free of resistive or (visco-elastic and or geometric) dissipative mechanisms. In case of the presence of such mechanisms, a complex valued term is added to the formulation of the wavefield, i.e., the function satisfying the wave equation. The transverse or shear wave impedance is defined as [PR15, p.105]

$$Z = \frac{\text{transverse force}}{\text{transverse velocity}} = \frac{F}{\nu}$$
(2.6)

After the introduction of Z, the distribution of energy along a vibrating string shall be considered. At all points of the transverse motion, a change of kinetic and potential energy can be observed. Both energies are expressed as:

$$E_{kin} = \frac{1}{2}\rho dx \left(\frac{\partial y}{\partial t}\right)^2 \tag{2.7}$$

$$E_{pot} = T(ds - dx) = T\{[1 + (\frac{\partial y}{\partial x})^2]^{\frac{1}{2}} - 1\}dx = \frac{1}{2}T(\frac{\partial y}{\partial x})^2dx$$
(2.8)

where T is the tension which does the work by extension of an element dx to a length ds during the vibration. If a wave propagates in first order of small changes of the Y-position of the string along the vertical direction, for each longitudinal position X, T is considered as a constant when the change is of second order. Consequently, kinetic and potential energies occupy equal, instantaneous values of energy at all points. [PR15, p.107 et. seq.] [Gra91]

The vertical displacement of one end side of the string along the Y directions leads to a progressive wave of other Y displacement along the length of the string, at the successive X positions. If the other end of the string is, e.g., free to move vertically, such progressive wave is entirely reflected at an infinite impedance with π phase change due to the reflection at the boundary. The same happens in the case of a fixed boundary conditions. In linear elastic media, the progressive wave incident to the right end side of the string overlaps with

the wave reflected by such end side. By the super-position of many harmonic waves produced by multiple reflection at both end sides (boundaries), a standing wave will be formed when a monochromatic wave of a frequency ω is present. The vertical position y(x,t) of the string due to the forward progressive harmonic wave and to the backward one created by the reflection at x = l, where l is the total length of the string (thin rod) can be described at any point in time and space as

$$y = ae^{i(\omega t - kx)} + be^{i(\omega t + kx)}$$
(2.9)

y(x,t) of Eq. (2.13) must satisfy a scalar wave equation as the (2.5) one, with the only difference that the square of the wave velocity, c^2 , is equal to the ratio between the tension T and the mass density ρ . If y = 0 at x = l (fixed boundary condition at that side of the string) or the force there is 0 (free boundary condition), then the values of the angular frequency are limited to

$$\omega_n = \frac{n\pi c}{l} \quad \text{or} \quad \nu_n = \frac{nc}{2l} = \frac{c}{\lambda_n}$$
(2.10)

where n is a non-zero integer number and $\nu_n \equiv \frac{\omega_n}{2\pi}$ is the temporal frequency in units of Hz or multiples thereof. The multiple reflections at the sides of the string, with different boundary conditions, lead to the build up of a spatial pattern of the vertical displacement of the string points which is sinusoidal with a finite and discrete set of possible spatial frequencies given by the inverse of λ_n or by $k_n \equiv \frac{2\pi}{\lambda_n}$, the latter playing in space the same role the angular frequency plays in time. These frequencies are called normal frequencies or eigenfrequencies or resonance frequencies of transverse waves in a finite string. Longitudinal waves propagating in a finite thin elastic rod subjected to similar boundary conditions also generate standing waves with resonance frequencies also dependent only upon the length l of the rod and the longitudinal phase wave velocity c of the medium, itself dependent upon the Young modulus and the mass density. The resonance frequencies of such thin rod are defined by an equation identical to (2.14). Thereby, the possible wavelength of a standing wave/resonance vibration is such that an integer multiple of its half equals the total length of the string (rod). This integer multiple n is called the order of the existing standing wave or of resonance. Nodal points (amplitude = 0 for a standing wave) are found where the progressive wave has equal and opposite amplitudes generated by complete reflection at the boundary. A reflection of the wave is called complete when all the energy associated with the incident wave is transferred to the reflected one. In reality, a complete reflection of waves is not always achieved so that nodal points are ambiguous. Therefore, the term standing wave ratio was developed to describe the degree of reflection and of unambiguity of nodal points. Mathematically, this ratio expresses the relation between minimum and maximum amplitudes in standing wave system, where the maximum amplitude is $A_1 + B_1$ and the minimum one $A_1 - B_1$, whereby A the forward progressing wave and B the backward progressing wave is. The reflection coefficient r of the boundary of the medium is given by B_1/A_1 . Thus the standing wave ratio (SWR) results: [PR15, p.113 et. seq.]

$$SWR = \frac{A_1 + B_1}{A_1 - B_1} = \frac{1 + r}{1 - r}$$
(2.11)

2.1.3 General considerations

A standing wave (also called resonance vibration) in a finite specimen can be characterised in terms of how each point of the specimen oscillates about an equilibrium position in a specific direction (for linear polarized waves). The amplitude of such oscillation has a specific pattern of spatial distribution. If an oscillation of a single point in the specimen is considered, the boundary conditions determine the possible spatial distribution of amplitudes in the specimen, thus the maximum amplitude of oscillation of that point. The boundary conditions hence form the foundation for the choice of the applied theoretical model to describe the possible standing wave patterns (or resonance vibration modes). A system of coupled oscillators having different degrees of freedom is necessary. [PR15, p.69 et seq.] Here, in what follows, some basic terms and observable variables are introduced to characterise the resonance vibration modes of a finite specimen as described from the point of view dynamic (mechanical) systems, i.e., systems of coupled oscillators. One can imagine that each oscillator represents a lump of the actual finite specimen located, e.g. in 1D, at a certain position x.

A harmonic wave is built up by regularly developing, sinusoidal, oscillatory motion which can be damped or forced by outer influences. One characteristic of a simple harmonic wave is the independence of its amplitude [PR15, p.21 et seq.]. A repeating harmonic wave, as occurring in an infinite medium when the source of the waves is continuous in time, is called a vibration. As vibration is understood as a periodic back-and-forth motion of particles of an elastic body. At this point, the term resonance (or normal) mode shall be introduced. A resonance mode describes a standing wave state of excitation. In this state, a sinusoidal excitation at a specified fixed frequency reaches all components of the system, i.e., all the oscillators. By means of a resonance mode, the frequency of the sinusoidal oscillation of all the components is the same. The frequencies of the resonance modes are called normal frequencies or eigen-frequencies. Furthermore, a resonance mode possesses normal coordinates each corresponding to a degree of freedom of the overall type of vibration/oscillation. Based on the property, that resonance modes of vibrations are absolutely independent from each other, the energy of a resonance mode is never exchanged with that of another one. For example, a coupled pendulum shows a simple harmonic oscillation with two degrees of





freedom, one exhibiting mainly the stored potential energy, the other the aquired kinetic one. [PR15, p.72 et seq.] Furthermore, a resonance mode is associated to a continuous spatial distribution of maximum amplitude of vibration/oscillation which is due to the constraint of every particle having to follow a certain vibration type. [Gra91, p.40]

Depending on the boundary conditions, resonance mode exhibits in accordance with the type and order of the mode, a characteristic spatial pattern of maximum vibration amplitude. For example, the first longitudinal eigenmodes created in a thin elastic rod by a longitudinal excitation and by fixed boundary conditions are shown in figure 1. These modes exhibit a sinusoidal form in this given context, in that the amplitude of vibration/oscillation is always 0 at the two end sides of the rod. In contrast, a cosine-like pattern is observed under free boundary conditions.

At this point, another important concept and respective parameter for the characterisation of resonance

modes shall be introduced. So far, both from the continuous mechanics point of view and from the discrete one as well, only wave propagation and standing waves/vibrations/oscillations in a lossless material have been considered. "Lossless" means that all the energy input by the escitation to create the propating waves is stored within the specimen itself and gets continuously converted from potential energy to kinetic energy and viceversa. In such a finite specimen or system of oscillators, a resonance mode created by a continuous source of excitation leads to an amplitude of vibration which theoretically goes to infinite in correspondence of the position of maximum amplitude in space. That's because the excitation source continuously injects energy within the specimen, this energy not being lost but being fully converted in the vibration. In reality, any material has a certain degree of loss, due to different physical or geometrical mechanisms. Thus the vibration/oscillation amplitude is damped. In a damped motion, energy decays as a logical conclusion. If the resonance mode excitation is continuous in time, the lost energy is re-supplied by it, such that an equilibrium is achieved and the maximum amplitude of vibration/oscillation remains constant in time (but spatially different at the different position). As a guideline, a dimensionless value expresses the level of damping called quality factor or Q-value of resonance mode. The quality factor can be defined as [PR15, p.35-37]

$$Q = \frac{\omega' m}{r} \tag{2.12}$$

where ω' is the angular frequency, m the mass of the specimen/oscillator in resonance and r the resistive dissipating force. If r becomes small, Q can be considered as a constant:

$$Q = \frac{\omega_0 m}{r} \qquad with \quad \omega' \approx \omega_0 = \left(\frac{s}{m}\right)^{1/2} \tag{2.13}$$

where ω_0 is the initial frequency of the specimen/oscillator and *s* the spring constant. It can be shown, that, it relates with the ratio of $\frac{energy \ stored \ in \ system}{energy \ lost \ per \ cycle}$. Indeed, this ratio is contextually expressed as

$$\frac{energy \ stored \ in \ system}{energy \ lost \ per \ cycle} = \frac{E}{-\Delta E} = \frac{\nu'm}{r} \approx \frac{\nu_0 m}{r}$$

$$= \frac{Q}{2\pi}$$
(2.14)

Moreover, the quality factor is used in two additional situations, firstly as a value of power absorption bandwidth in damped systems closely driven to its resonant frequency and secondly as a factor of amplification of the displacement at resonance. [PR15, p.35 et. seq.] [Gra91]

In terms of resonance absorption bandwidth, the Q-value is defined by the following ratio which reveal information concerning the "sharpness" of the resonance. [PR15, p. 48 et. seq.]

$$Q = \frac{\omega_0}{\omega_2 - \omega_1} = \frac{\omega_0}{\Delta\omega}$$
(2.15)

In figure 2, the difference in ω is schematically shown. Commonly, the difference between ω_2 and ω_1 having exactly half of the resonance amplitude value is called the resonance absorption bandwidth, whereby ω_0 the middle of the peak is presenting the symmetry and the directive value to determine the peak hight and width as well. A resonance curve is a picture of a vibration initiated by an oscillating object which drives another system to oscillate with higher amplitude. Thus, the resonance vibration velocity amplitude is in figure 2 a concrete example for A. This value A can express rather a displacement, a resonance vibration velocity and the acceleration. Those are derivatives of each other.





Figure 2: Graph of average power regarding the quality factor and bandwidth [PR15, p.49]

Figure 3: Curves of displacement at resonance of low frequency response [PR15, p.60]

If the number of discrete oscillators increases in the limit of an infinite number of them, the mathematical description of resonance/vibration conditions gets the same as that used in continuum mechanics for describing resonances created by propagating waves. The change of relative displacements of neighboring oscillators is observed as waves which results from vibrating particles about their equilibrium position. [PR15, p.95].

2.2 Nonlinear elasticity of rocks and cement-based materials: basics and damage detection applications

2.2.1 Definition and considerations

In this Master Thesis, the exposition of the basics of the general theory of linear and nonlinear elasticity according to the theoretical framework provided by Landau and Lifshitz [LL70] is considered. What is presented in the book by Landau and Lifschitz is what is typically known as the classical approach to elastic nonlinearity. At first, some fundamental terms shall be clarified which relate to the general linear and (classical) nonlinear elasticity theory. Two key mathematical objects of the theory of elasticity are the strain tensor and the stress tensor. A deformation of a solid body is observed under the application of forces. This deformation is easily described as \bar{u} , the displacement vector. Briefly, it can be expressed as a change of relative position vector between two points or a change of length in an element during a deformation. Thus, each component u_{ik} of the strain tensor is defined as: [LL70]

$$u_{ik} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} + \frac{\partial u_l}{\partial x_i} \frac{\partial u_l}{\partial x_k} \right)$$
(2.16)

where $u_i, \forall i = 1, 2, 3$ represents a generic component of the displacement vector and Einstein sum convention is used (a sum over all possible values of the repeated index l is implicitly assumed). To be noticed in Eq. (2.19) is the term with the products of the partial derivatives. Such that is typically not presented in expositions of the theory of linear elasticity. Alone, such term leads to nonlinear wave equations. When a solid is in a state of equilibrium, the equilibrium is separated into thermal and mechanical equilibrium. If an external force is applied to the solid body, the arrangement of its molecules changes. Hence, the solid ceases its equilibrium. Reaction forces which tend to bring the body back to its original state of equilibrium are created, which constitute the elastic response of the body. These internal forces are denoted as internal stresses. The continuum of elasticity works on a macroscopic basis because the single, local molecular forces are considered, in theory, to balance themselves locally, just leading up to net macroscopic forces at the length scale of the entire body. Based on such assumption, only the total, macroscopic net force, i.e., the sum of all forces acting on a macroscopic scale, is considered. Such total force can be expressed for any whole volume of a specimen as an integral over overall volume according to Newton's second law:

$$\int F_i dV = \int \frac{\partial \sigma_{ik}}{\partial x_k} dV = \oint \sigma_{ik} df_k$$
(2.17)

In equation (2.17), σ_{ik} is the component of the internal stress tensor acting in direction *i* on a unit surface orthogonal to the *k* direction tensor. Equation (2.17) shows the correspondence between the bulk volumetric density of force acting on a lump of material with small volume dV and the partial derivatives of the internal stresses acting on its boundary surface, i.e., the components of the stress tensor σ_{ik} . Any wave equation can thus be simply obtained by applying Newton's second law written for such lump of material using volumetric density of acceleration and of forces:

$$\rho \cdot \frac{\partial^2 u_i}{\partial t^2}(\bar{x}, t) = \frac{\partial \sigma_{ik}}{\partial x_k}(\bar{x}, t), \forall i = 1, 2, 3$$
(2.18)

where $\bar{x} = (x_1; x_2; x_3)$ indicates the position vector of the center of the small lump of material with volume dV and t indicates time and such functional dependence on space-time is introduced to remind that both the displacement vector and the stress tensor are fields, i.e., depend on space-time. The final version of a scalar wave equation should depend only on the components of the displacement vector field. Such version is obtained by inserting in the previous Eq., the equation of state (EoS, also called stress-strain constitutive), which expresses the dependence of each component of the stress tensor on the components of the strain tensor. Such stress-strain EoS is a key feature of a given category of materials, from the mechanical point of view. The general expression of a stress-strain EoS is obtained by basic equilibrium thermodynamics principles. When the thermodynamics of the deformations are taken into consideration, the term expressing the work done by the internal stresses, here called $\delta R = \sigma_{ik} du_{ik}$, has to be introduced. To describe the small change in entropy, dS, is needed as well. Remembering that G = E - R - TS = F - R, where E is the internal energy of the lump of material, F is its Helmholtz free energy and T is the absolute temperature and using the assumption that the elastic deformation occurs isothermally, it results that $dG = d\mathbf{E} - d\mathbf{R} - T d\mathbf{S}$

- s dT = -S dT. Since the elastic deformation consequent the application of external forces is assumed to bring the lump of material back to a thermodynamic equilibrium via an isothermal thermodynamic transformation, the differential of the Gibbs free energy dG is assumed to be equal to 0. It can be also described as [LL70, p.9]

$$dE = TdS + dR = TdS + \sigma_{ik}du_{ik}$$
(2.19)

This equation represents the fundamental thermodynamic (Gibbs-Duhem) relation for elastically deformed bodies. It is nothing but the expression of the 1st principle of equilibrium thermodynamics for isothermal thermodynamic transformations. It can also be written as

$$dF = dR = \sigma_{ik} du_{ik} \tag{2.20}$$

for isothermal thermodynamic transformations. It says that the components of the stress tensor can be obtained by deriving the Helmholtz free energy in respect to the correspondent component of the strain tensor, or

$$\sigma_{ik} = \left(\frac{\partial F}{\partial u_{ik}}\right)_T \tag{2.21}$$

where, T indicates the condition of a constant temperature. The macroscopic model is considered being rooted in equilibrium thermodynamics and assumptions of elastic deformations corresponding to isothermal thermodynamic transformations. Thereby, the hypothesis can be formulated

$$F = F(u_{ik})_{i,k=1,2,3} \tag{2.22}$$

When $F(u_{ik})$ is expanded in power series about 0, it is called Taylor expansion of $F(u_{ik})$ about 0, Maclaurin expansion or $F(u_{ik})$ in multi-dimensional scale:

$$F(u_{ik}) = F_0 + \frac{1}{2!} C_{iklm} u_{ik} u_{lm} + \frac{1}{3!} C_{iklmno} u_{ik} u_{lm} u_{no} + \frac{1}{4!} C_{iklmnopq} u_{ik} u_{lm} u_{no} u_{pq} + \dots$$
(2.23)

Here, the expansion is implied to show the first elastic constants containing important information concerning the corresponding elasticity theory and the behaviour of a material. Where $C_{iklm} = 2^{nd}$ order elastic constants, $C_{iklmno} = 3^{rd}$ and $C_{iklmnopq} = 4^{th}$. When small strains u_{ik} are assumed, linear stress-strain equations of state are formulated by cutting $F(u_{ik})$ to the term with second order powers:

$$F(u_{ik}) = F_0 + \frac{1}{2!} C_{iklm} u_{ik} u_{lm}$$
(2.24)

where, linear wave equations result describing linear elasticity.

$$\sigma_{ik} = \left(\frac{\partial F}{\partial u_{ik}}\right)_T = C_{iklm} u_{lm} \tag{2.25}$$

By application of theses equations to a 1D medium as an elongated thin rod, the following equations are formed:

$$F = F_0 + \frac{1}{2}Y_0\varepsilon^2 \tag{2.26}$$

$$\sigma = \left(\frac{\partial F}{\partial \varepsilon}\right)_T = Y_0 \varepsilon \tag{2.27}$$

where, Y_0 is the linear Young's modulus. By applying high strain amplitudes, the stresses in a material increase because inhomogeneties and microcracks react to the oscillation and the nonlinear behaviour responds. When u_{ik} is not considered as infinitisimal small, the nonlinear stress-strain equations of state can be derived by reducing the Taylor series to the term of forth order powers of u_{ik} . The forth term is chosen as cutting limit because of the necessity of those terms to predict resonance frequency shifts with increasing strain amplitude.

$$F = F_0 + \frac{1}{2!}C_{iklm}u_{ik}u_{lm} + \frac{1}{3!}C_{iklmno}u_{ik}u_{lm}u_{no} + \frac{1}{4!}C_{iklmnopq}u_{ik}u_{lm}u_{no}u_{pq}$$
(2.28)

$$\sigma_{ik} = \left(\frac{\partial F}{\partial u_{ik}}\right)_T = C_{iklm}u_{ul} + \frac{1}{3}C_{iklmno}u_{lm}u_{no} + \frac{1}{6}C_{iklmnopq}u_{lm}u_{no}u_{pq}$$
(2.29)

whereby, the nonlinear elasticity is described. When the nonlinear wave equations are adopted to a 1D elongated, thin rod, the nonlinear, generalised Young's modulus dependent on strain can be determined.

$$F = F_0 + \frac{1}{2!}Y_0\varepsilon^2 + \frac{1}{6}Y_1\varepsilon^3 + \frac{1}{24}Y_2\varepsilon^4$$
(2.30)

$$\sigma = \left(\frac{\partial F}{\partial \varepsilon}\right)_T = Y_0 \varepsilon + \frac{1}{2} Y_1 \varepsilon^2 + \frac{1}{6} Y_2 \varepsilon = Y_0 \left(1 + \frac{Y_1}{2Y_0} \varepsilon + \frac{Y_2}{6Y_0} \varepsilon^2\right) = \varepsilon$$
(2.31)

$$\sigma = Y * \varepsilon \tag{2.32}$$

whereby, Y is

$$Y = Y(\varepsilon) = Y_0(1 + \beta\varepsilon + \delta\varepsilon^2)$$
(2.33)

where
$$\beta = \frac{Y_1}{2Y_0} =$$
normalised cubic Young's modulus (2.34)

and
$$\delta = \frac{Y_2}{6Y_0} =$$
 normalised quadratic Young's modulus (2.35)

The resonance frequency shift of the first longitudinal mode shows a dependency on ε as well. By this dependency, the relation between resonance frequency shift and nonlinear gaeneralised Young's modulus can be shown:

$$|\frac{\Delta f}{f_{lin}}| \propto \delta * \varepsilon^2 \tag{2.36}$$

whereby, the order of ε expresses a predicted scaling behaviour between the resonance frequency shift and ε which have been differntly observed in SIMONRUS measurements with longitudinal modes of elongated thin rods of stones and concrete. Therefore, this description of the relation is more likely:

$$|\frac{\Delta f}{f_{lin}}| \propto \varepsilon \tag{2.37}$$

In regard to the examined materials, the mesoscopic theory shall be included in considerations. Hence, the nonlinear dependent Young's modulus is expanded by non-classical terms:

classical nonlinear elasticity:
$$Y(\varepsilon) = Y_0(1 + \beta \varepsilon + \delta \varepsilon^2)$$
 (2.38)

non-classical nonlinear elasticity:
$$Y(\varepsilon) = Y_0(1 + \alpha \Delta \varepsilon + sign(\dot{\varepsilon})\varepsilon)$$
 (2.39)

$$Y(\varepsilon) = Y_0(1 + \beta\varepsilon + \delta\varepsilon^2 + \alpha\Delta\varepsilon + sign(\dot{\varepsilon})\varepsilon)$$
(2.40)

whereby, the classical part is often neglected in mesoscopic theory.

Another essential term for elasticity occupies Hook's law. For application of the general equation of thermodynamics, the free energy F has to be known. In an isotropic body in constant conditions, F can be generalised as

$$F = F_0 + \frac{1}{2}\lambda u_{ii}^2 + \mu u_{ik}^2$$
(2.41)

Whereby, the quantaties λ and μ represent the Lamé coefficients. F can also be expressed in terms of pure shear and hydrostatic compression. If it is considered in dependence of those terms, the bulk modulus (K) or modulus of compression will appear in this context which is related to the Lamé coefficients by

$$K = \lambda + \frac{2}{3}\mu \tag{2.42}$$

By consideration of the nonlinear elastic behaviour of cement-based materials and rocks, the term hysteresis has to be introduced. When the solid is measured quasi-statically, a stress-strain curve is detected revealing properties of elastic behaviour.

In figure 4, the development of loading and unloading forces have been detected for Berea sandstone expressed in stress and strain. The upper curve shows the process of loading and the lower one of unloading. The space in between both curves indicates the energy loss caused by internal friction leading to the observation of nonlinear elastic behaviour.

The nonlinear elastic behaviour can be determined by increasing driving amplitudes. Through the excitation with growing energy, internal damages and microcracks start to distort the propagating wave by deformation through oscillation. Therefore, the resonance frequency of higher driving amplitudes shift



Figure 4: Stress-strain curve of Berea sandstone showing hysteresis [OJ01]

to lower values. The relative frequency shift $\left|\frac{\Delta f}{f_{lin}}\right|$ indicates a certain nonlinearity.

2.2.2 Relationships between nonlinear elastic behaviours and water saturation degree: the role of water in rocks and cement-based materials

According to the basic assumptions of the non-linear mesoscopic elasticity theory and the experimental evidence from corresponding measurements, the interstitial spaces between "grains" in unconsolidate and consolidate granular materials are the mesoscopic structural features leading to the correspondingly observed and predicted non-linear elastic behaviours which are not explainable by the anharmonicities of the crystalline grains themselves. As mentioned before, these interstial spaces may have different degrees of porosity, different pore size ranges and pore size distributions. For example, the inter-grain spaces in sandstones or limestones are filled with a "cementing" matrix with very different poromechanical properties compared with the cement matrix binding together the aggregates in concrete. Despite the differences, since such cementing matrices are thought (and shown, in certain cases) being responsible for the macroscopic non-linear elastic behaviours observed, one should expect that changes in their poromechanical properties and/or states should significantly affect the macroscopic non-linear elastic properties. Among all the poromechanical properties, the saturation degree is clearly a very important one which easily varies in cement-based materials.

The saturation degree in such materials obviously varies in any of their practical applications due to boundary conditions, e.g., due to the possibility of water, once evaporated, to be transported towards the outside environment due to unsealed boundary surfaces of a specimen. Such transport of water vapor leads to a decrease in saturation degree, typically called drying, and correspondent shrinkage which can create cracking, as fully explained in Section 2.3. Drying shrinkage and cracking not only alters the local saturation degree, changing the poromechanical properties of the inter-grain interstistical spaces/cementing matrices. They may also create new/more of such spaces in the form of (micro-)cracks, which, as mentioned in Section 2.2.1, are considered as an example of mesoscopic features responsible for non-linear mesoscopic elastic effects. In addition to the creation of new interstistical spaces, local changes in water saturation degree change the balances between pore-scale forces acting on such spaces. There are several types of such pore-scale forces and their balances or unbalances have been called for to explain why a change in saturation degree leads to change in non-linear mesoscopic elastic parameters. Beyond basic understanding of couplings between poromechanical processes and features and non-linear mesoscopic elastic ones, a complete understanding of how and why a change in saturation degree can change such non-linear effects/properties has a practical relevance as well: if, e.g., a non-linear mesoscopic elastic modulus is used as a "cracking" index, how much is its change, e.g., in drying concrete is due to the actual creation of new cracks and how much is due to other poromechanical effects which are not related with the creation of new interstitial porosity in the form of cracks? Can such parameter as a cracking index be reliably used when a porous material as concrete or a stone undergoes a change in saturation degree or only when cracking occurs in the absence of changes in saturation degree? These are some of practical questions that have been addressed in this Master Thesis work.

By explaining the influence of water saturation degree on nonlinear elastic behaviour, two internal forces shall be briefly named (further clarification in Section 2.3) and their development during drying explained. Hence, the capillary forces are sensitive to internal RH changes, the capillary forces increase with diminishing saturation degree resulting in a "closure" of cracks, reduction of surface at interstitial interfaces and of volume fraction of mesoscopic features causing nonlinear mesoscopic effects. Moreover, the disjoining pressure is responsible for the separation of opposite surface of cracks and further interstitial inter-grain features which is reduced by decreasing water saturation degree.

A further parameter influencing the nonlinear elastic behaviour and water saturation degree is the pore network and their size distribution. Depending on the amount and size, water can evaporate more easily and less microcrack evoking. For example, in cement-based materials the distribution of pores are more widely compared to sandstone by means of higher capillary forces, microcracking due to the process of drying and longer drying times. Those resulting effects lead to an increase in nonlinear elastic behaviour with decreasing water saturation degree for cementitious solids.

Furthermore, the dependence of the nonlinear parameter on moisture relates to a alteration of the interfaces between (poly-)crystalline grains and cracks/interfaces upon changes in saturation. This can be explained

inter alia by the solid fluid pressures. Those pressures contain molecular adsorption forces at the pore walls, capillary pressures and interlayer fluid pressures based on interlayer hydrate water in nanopores. The microscopic capillary pressure is described by means of Kelvin's law and relates as a decreasing function of pore relative humidity. Concluding, microscopic capillary pressure diminishes with growing degree of saturation. Morever, the microscopic contraction forces decreases resulting in expansion of the solid with an increasing saturation, as well as active nonlinear and/or hysteretic microinhomogeneities and the possibility of state change grow. [VCJZ02] [PGM10]

2.3 Drying shrinkage in cement-based materials and their behaviours

2.3.1 Overview

The presence of free water and related thereto the changes in moisture content within the pore structure are a common phenomena in cement-based materials. These changes cause dimensional changes and corresponding tensile stresses which can provoke internal cracking. In general, two mechanisms are distinguished being responsable for internal moisture changes. Firstly, an autogeneous shrinkage occurs during cement hydration, in particular at low water-to-binder ratio (w/b < 0.4), because of the smaller volume occupied by chemically-bound water compared with the free one. Such volumetric differences for water in different molecular states results in an overall, intrinsic reduction in the volume of the phases (cement + aggregates + water + additives), usually called chemical shrinkage. Such reduction means that some parts of the original space inside the pore space becomes empty, corresponding to the successive establishment of liquid water-air interfaces associated with capillary pressure fields which signify a local decrease in saturation degree of the pore space and may lead to cracking. Secoundly, water evaporation and water vapor diffusion towards the external environment (if at lower relative humidity) through unsealed surface boundaries contributes as well to the process of water removal from the cement matrix, concretely of the pore structure. This process can result in substantial shrinkage which is caused by the induction of free surface energy changes for newly formed interfaces between liquid water, empty pore space, i.e., air, and the solid phases. Such changes lead to the creation of highly heterogeneous spatial distributions of disjoining pressure and capillary pressure. Moreover, moisture content gradients are developed as regions closer to the boundary surfaces through which the water vapour evaporates release moisture faster. Spatially heterogeneous gradients in moisture content lead to highly heterogeneous and localised tensile stresses, resulting from super-positions of the highly heterogeneous capillary and disjoining pressure fields. These stresses enhance tensile cracking, especially in materials with low diffusion rates. [EPB+15] [Sch90] [BPP99] [SBM03] [Loc00, p. 302]

2.3.2 Mechanisms

The process of drying is subdivided in three stages: an initial stage, a constant (drying) rate period and a falling rate period. During the first stage, liquid water flows through the pore system, towards the evaporation boundary surface, in correspondence to the formation of an overall gradient in capillary pressure. Simultanously, deformations of the solid network and dilation of the pores are produced by this gradient in capillary pressure. One of the shrinkage-provoking forces is the capillary pressure. During the evaporation of the liquid from the pores, a solid/vapour interface is formed which has higher surface energy compared with the solid/liquid interface. A new, liquid water/air interface results from such surface energy difference, typically called meniscus. As inhibition of surface energy increase, interior liquid advances to cover part of the newly formed interface. Due to the reduction of liquid volume in contact with the solid in the pore region still completely saturated, the meniscus becomes curved. The radius of curvature, r, of such water/air curved interface is related to the capillary pressure (P) [Sch90]:

$$P = -2\gamma_{LV}/r \tag{2.43}$$

where γ_{LV} represents the liquid/vapour interfacial energy or surface tension and r the radius of curvature. The liquid is in tension when the center of the cuvature is located in the vapour phase. Hence, a maximum capillary pressure is achieved when the curvature radius of the meniscus fits into the pore. In the theoretical model, the pore is described as cylindrical space. An indicating factor of the maximum pressure is the surface-to-volume ratio of the cylindrical pore with radius R, called P_R and $S_p/V_p = \frac{2}{R} = \frac{2}{rcos(\theta)}$ which can be derived as [Sch90]

$$|P_R| = \frac{\gamma_{LV} \cos(\theta) S_p}{V_p} = \frac{(\gamma_{SV} - \gamma_{SL}) S_p}{V_p}$$
(2.44)

$$\frac{S_p}{V_p} = \frac{S\rho_s\rho}{1-\rho} \tag{2.45}$$

In the equation (2.44), the interfacial energies γ_{SV} (solid/vapour) and γ_{SL} (solid/liquid) are introducted and liaised with the contactangle θ . The equation (2.45) expresses the surface-to-volume ratio as a function of the specific surface area S, the relative density ρ and the density of the solid skeleton ρ_S . [Sch90] [Sch15] [SBM03] [BPP99]

The second shrinkage-provoking force is an osmotic pressure Π . In cement-based materials, the pore system is permeated by not only pure water, rather and mainly by a water-based solution. The creation of concentration gradients develop osmotic pressure, which expresses the difference in chemical potential between to liquids (e.g. pure water - salt solution). By consequence in the presence of drying, the salt concentration near the drying surface increases by the evaporation of the solvent (if the pores contain a electrolytical solution). Therefore, the liquid solvent tends to diffuse to evaporation boundary surface to diminish the concentration gradient, which causes additional tension in the liquid through the reduction of the internal liquid volume. Depending on the pore size, either the diffusive flux and the counterflow towards the interior show a similar force, no additional stresses occur, or smaller pores support a flow and tensile forces can be locally produced which can lead to shrinkage by the balancing compression.

The shrinkage-provoking force types include the disjoining pressure as well. The short-range capillary forces associated with the menisci tend to bring solid surfaces closer together. By decreasing distances between the solid surfaces, electrostatical repulsive forces start to become larger and larger, opposing the local deformations created by the capillary forces. As a result, a flow of the pore liquid may occur from the swollen interior of the cement hydration products, especially the amorphous ones as the calcium-silicate-hydrates, which have typical layered structures, towards their exterior layers, enabling the solid surfaces to move farther apart. Hence, an osmotic flow may result, led by a gradient in the chemical potential of the liquid phase. Capillary forces are expected to exhibit a more significant influence on shrinkage, especially in clays and

cement-based materials, due to the predominance of nanometer-scale pores in these materials and the layered nano-structures which characterise them. [Sch90] [RG17]

The fourth type of force is called moisture stress or moisture potential (ψ), which describes the partial specific Gibbs free energy of a liquid in a porous medium:

$$\psi = \left(\frac{R_g T}{\rho_L V_m} \ln(\frac{p_V}{p_0})\right) \tag{2.46}$$

The included parameters express the follwing: ρ_L the density of the liquid, V_m the molar volume of the liquid, R_q the ideal gas constant, T the temperature, p_{V} the vapour pressure of liquid in the system and p_0 the vapour pressure over a flat surface of pure liquid. The moisture potential includes partially other factors, since the vapour pressure is also influenced by the capillary pressure, the osmotic pressure, the disjoining pressures and adsorption forces. Nevertheless, it is often used in soil science although the concentration gradients causing diffusion are mostly neglected when explaining water transport due to evaporative drying just by the moisture potential gradients, which evokes a less accurate description of the process. [Sch90].

The actual process of evaporative drying mainly starts with the Constant Rate Period (CRP) (Fig. 5). Thereby, the evaporation rate (\dot{V}_E) plays a less significant role as during the falling rate period, because the decrease of vapour pressure is negliglible in the first stage, besides in some cement hydration products with small pores. The evaporation rate is defined as:



Figure 5: Stages of Drying by Scherer [Sch90]

$$\dot{V}_E = k(p_V - p_A) \tag{2.47}$$

where p_A is the ambient vapour pressure and k a factor depending on the temperature and pore space geometry. The reason why the evaporation rate plays a secondary role in driving the drying kinetics is that, during the CRP, the boundary surface is connected with the region within the specimen still fully saturated via networks of liquid clusters, sometimes also called films, along which it is believed the liquid is quickly transported, by capillary force gradients, close to the surface, where it can evaporate. Such network of liquid films supply continuously and rapidly liquid water ready for fast evaporation directly at the surface. Such continuous supply allows reaching a constant and high rate of evaporation. A vapour boundary layer forms over the surface, which builds up an equilibrium concentration of vapour. As a result of such continuous and fast evaporation. The body cools down and the process equilibrates at reached wet bulb temperatur (T_W). A compression in the liquid is built up, due to tension and hydrostatic pressure in the liquid being supported by the solid phase. During such state of drying, the network stiffens increasingly, as new contact points between the solid surfaces form and a consequent reduction of the porosity occurs. The capillary pressure increases in the bulk of the liquid is accompanied by a decrease of the radius of curvature deepening of the meniscus. When such radius achieves a value close to the characteristic pore size of the structurally layered cement hydration products, the maximum tensional force is achieved. At this point, some of the networks of liquid films start to get disrupted, because of smaller and smaller menisci at the interfaces. When an increasingly smaller number of such networks do not percolate anymore from the completely saturated region inside the specimen to the evaporation surface, the transport of liquid water via capillary forces starts to get reduced. From that point on, the specimen drying is driven not only and mainly by the evaporation of the liquid water which has been transported to the boundary surface but more and more via evaporation and diffusion of the vapor phase from the interior to the boundary surface through the pore space. Since diffusion is much slower than liquid transport driven by capillary forces, the drying rate starts to monotonically decrease. During this stage, the shrinkage is limited to the volume of evaporating liquid. The term "critical point" describes the end of the CPR where the radius of the meniscus is small enough to be compatible with the smallest pores in the layered hydration products. [Sch90]

The FRP is itself typically divided into distinct sub-periods. The transition from the CRP to the first FRP is characterised by a strong reduction of the evaporation rate and by the increase of the temperature above the wet bulb temperature. The remaining clusters of liquid are still evaporating. As a consequence, the temperature remains below the ambient temperature. Moreover, such liquid clusters are arranged in a so called "funicular" configuration, which still allows flow. As the second FRP is approached, menisci withdraw more and more into the bulk of the solid. However, the liquid may still advances to the exterior surface along the few remaining percolating networks of liquid clusters, as long as the liquid flux and the evaporation rate are comparably equal. Under these conditions it is said that the funicular condition prevails. When the distance between the exterior and the so called drying front (a sort of surface inside the specimen separating a bottom region still completely saturated from one above partially saturated) achieves a certain length scale, the capillary pressure gradient responsible for the liquid transport towards the exterior surface critically diminish as such it cannot overcome anymore the resistance to the liquid displacement due to gravity and viscous forces. This is the point when the liquid flux decreases enough not to allow the survival of any percolating network of liquid clusters. Such networks start depercolating and break into isolated liquid pockets, if the body shows a sufficient cross-section and the liquid flux decelerates effectively. At this stage, the evaporation inside the solid. The exterior surface achieves ambient temperature and the rate of evaporation is more desensitised to outer conditions. In layers close to the exterior, a distinction between the funicular condition and a pendular one for the isolated liquid clusters can be made. The pendular condition is characterised by the vapour equilibrium with the isolated liquid pockets and adsorbed films. The total stress on the solid network is significantly reduced by the retreat of the fully saturated region so that the specimen can expand slightly. Simultaneously,

new strains are produced as a result of the solid network compression in the partially saturated regions. With ongoing drying, the unsaturated regions inhibit further the contraction which increases the tension in the porous partially saturated regions [Sch90].

During the overall process of drying, cracking occurs. Different models have been used to explain this phenomenon. In general, it has been observed that the likelihood of cracking increases with the thickness of the specimen or at high evaporation rates driven by very small environmental relative humidity values. Moreover, fracture normally appears at the critical points, at the transitions from the CRP to the 1st FRP and from the 1st FRP to the 2nd one,when the vapour/liquid interface is shifted into the specimen. Two models have been proposed, a macroscopic model [Sch90] and a microscopic one [Sch90]. The macroscopic approach explains cracking by stresses resulting from a pressure gradient in the liquid. The microscopic model considers cracking as a product of pore size distribution. The liquid recedes into the interior starting from the largest pores and continuing with the next smaller one, after the critical points. Therefore, the capillary forces in neighbouring small pores deforms the pore walls and cracking occurs as a result. [Sch90] [Sch15] [SBM03] [BPP99] [Pic56]

2.3.3 Influences

According to the microscopic model [Sch90], porosity, or rather pore size distribution, has a great impact on cracking induced by drying. One parameter directly influencing drying shrinkage and cracking in cement-based materials is the water-to-binder ratio (w/b ratio). Different researches have considered this influence and shown that, by increasing the w/b, the amount of capillary pores increases and the water transport changes correspondingly. In general, it is considered that shrinkage is reduced by decreasing w/b ratios. However, an augmenting microcracking is recognised at very small w/b values, (e.g., w/b = 0.25). Such microcracking increase is mainly caused by autogeneous shrinkage itself, an effect very well known and characterised in the context of the development of high performance concrete (HPC) and ultra high performance concrete (UHPC). [EPB+15] [BPP99]

Parameters related with the external conditions, like temperature and especially relative humidity, influence the drying shrinkage process significantly. The higher the environmental relative humidity is, the more easily is the liquid water transported through the pore space and the more funicular regions are obtained. By diminishing the external relative humidity, the first critical point (transition from CRP to 1st FRP) occurs earlier, when the hydrated cement-based system has reached lower tensile and compressive strength values, and larger stresses are developed at levels which may overcome the strength ones. Thus, the solid strives to achieve its equilibrium with the outer system so that at lower relative humidity values higher stresses are produced which can result in cracking because they may easily overcome the correspondingly achieved low strengths. [BPP99] [EPB⁺15] [Sch90]

Moreover, the effects of the binder paste volume and of the aggregates content on shrinkage are considered having a great influence. Based on Pickett's work [Pic56], shrinkage is reduced by increasing the aggregate volume fraction because cracking occurs in the paste volume, especially in C-S-H gel, and by a smaller volume the substance which cracks primarly is limited. [EPB⁺15] [BPP99] [SBM03] [Pic56]

Further influences can be the structure of the pore network, mechanical and thermal properties of the paste and of the aggregates as well, size and geometry of the specimen and the curing age. [EPB⁺15] [BPP99] [SBM03] [Pic56]

2.3.4 Rocks versus cement-based materials

Excluding cases where drying shrinkage is reduced as much as possible by sealing the boundary surfaces of specimens/structures in contact with air or by external curing with water sprayed/poured on top of them, both of which are expensive practices, drying shrinkage and respective cracking is one of the most common early shrinkage and cracking processes badly affecting the durability properties of cement-based materials. Nonlinear elasticity measuring methods have been pointed out as non-destructive evaluation methods potentially equipped with higher sensitivity than linear elasticity ones for the detection of early age cracking in cement-based materials. However, since several complementary and sometimes antagonist mechanism takes place during drying in porous materials, any understanding of the evolution of the nonlinear elastic moduli during it is necessary for intepreting their results.

Rocks and cement-based materials differ from each other in their behaviour during drying and also in the dependence of their nonlinear (mesoscopic) elastic moduli on the saturation degree, during a drying process. Despite both of them exhibit mainly nonlinear mesoscopic elastic responses instead of classical nonlinear ones, their micro- and nano-structural differences lead to such different dependences. First of all, the pore size range and distribution may differ significantly for the two types of materials. Since these two features significantly impact the process of drying, it is to be expected that they may lead also to distinct relationships between nonlinear elastic moduli and saturation degree. In cement-based materials, the pore size spans a very broad in range, from a few nanometers to millimeters, whereby rocks, so far used for nonlinear meso-scopic elasticity measurements, exhibit narrower ranges, mainly between tens of nanometers to hundreds of microns. The types of investigated rocks, mainly sandstones, are thought of getting "compacted" at low saturations (<20%) by the capillary forces associated with the liquid water-air menisci. By the increasing saturation, a reduction of the microscopic capillary forces results in less compaction and eventually in an expansion of the solid matrix and a reduction of the macroscopic stiffness. As a consequence of local expansion, it has been hypothesised that the micro-inhomogeneties, like microcracks and asperities, may get sort of "deactivated" with increasing saturation degree. [VCJZ02]

Figure 6 shows the evolution during drying of one nonlinear mesoscopic elastic modulus, called α , measured by nonlinear resonant ultrasound spectroscopy (see Section 3.1 for its definition) with decreasing saturation degree. A global maximum value was achieved, for two distinct sandstone types, at saturation degree values of about 10% - 20%. For lower and decreasing saturation values, α decreased. At higher but decreasing saturation values α increased [VC]Z02]. The interpretation offered by the author of that study was that a maximum lpha value at about 10% - 20% saturation was achieved because of a balance between compacting capillary forces and disjoining pressure ones was achieved as such to keep the micro-cracks and grain boundaries open enough for maximising their contribution to the macroscopic scale nonlinear elastic response. At higher saturation degrees the expansive forces due disjoining pressure overcame the capillary ones while for lower saturation the viceversa occured, with consequent closure of the micro-cracks. No additional micro-cracking should have occurred for decreasing saturations, below 10% - 20%, which would have led to an increase of lpha. A completely different trend with decreasing saturation degree has been reported for cement-based materials in two works [PGM10] $[EPB^+15]$. Figure 7 shows the evolution with decreasing saturation degree for a nonlinear (mesoscopic) elastic modulus, also called α , with similar meaning as the one measured in the work of Van den Abeele et al [VCJZ02]. Cement-based materials are characterised by a much more inhomogenous structure, wider pore size distribution and larger porosity, with much higher relative fraction of nanometer



Figure 6: Development of hysteric nonlinearity at increasing saturation degrees in sandstones [VCJZ02]



Figure 7: Development of nonlinear parameter at different water saturation levels in concrete [PGM10]

scale pores, compared with the sandstones. Therefore, first of all, they need longer time to achieve equilibrium, because of slower diffusion processes. Moreover, the produced stresses by the withdrawn liquid lead to greater hysteric effects, nonlinearity and microcracking. Especially at low saturation, the behaviour differs strongly from the sandstones, because of the likely predominance of the capillary forces which not only overcome the disjoining pressure effects but also increase the microcrack volume fraction, reaching far larger values than what achievable within the sandstone due to larger volumes of smaller pores. Thus, the nonlinearity increases significantly in concrete, in particular at low and decreasing saturation, in strong contrast, with what exhibited by the sandstones. [Sch15] [VCJZ02] [PGM10]

2.3.5 Influence of Shrinkage Reducting Admixture (SRA) on drying processes in cement-based materials

A SRA is described as a non-ionic surface-active admixture which contains, on a molecular scale, both a hydrophilic and a hydrophobic group [RJ05]. Because of this molecular structure, the surface tension of water (or rather pore solution) gets reduced expected that the usage of SRA should result in faster evaporation rates. As reported by Bentz et al. [BGH01], pure water in a glass evaporates slower than water mixed with SRA or the SRA itself. In contrast, when they compared two different mortar or concrete mixtures (one with SRA and one without), the cemetitious materials without SRA showed a faster drying rate than the one with SRA, so the opposite was observed as it has been expected. In further research, a cement paste showed a non-uniform drying during the first 13h characterised by a clear drying front which disappeared after those interval of time [BGH01]. These phenomena can be explained by different approaches: [BGH01] [RJ05] [RGC06] by reducing the capillary pressure of the pore solution, via diminishing the surface tension, SRA inhibits capillary suction and distributes the solution more homogeneously, so that outer layers dry as fast as inner layers of the material. Due to this mechanism, the cement-based materials takes a longer time period to dry.

Despite the difference in drying kinetics, which makes it difficult to compare results for specimens of cementbased materials cast with and without SRA, the usage of SRA offers the opportunity to investigate the changes, during drying, in the nonlinear (mesoscopic) elastic properties of a porous system which more significantly resembles, pore structure-wise, a normal (i.e., cast without SRA) system but whose nonlinear elastic properties should be less affected by the increase in micro-crack volume fraction, because of a smaller amount of shrinakge cracking.

The hypothesis made at the beginning of this Thesis was the usefulness of comparing the evolution of nonlinear elastic moduli in drying specimens cast with and without SRA in order to evaluate, with the former specimens, mainly the effects of the decrease in saturation degree, without being predominantly affected by the micro-cracking, and the effects of such decrease coupled with the micro-cracking in the latter specimens. A few experimental studies about shrinkage also reported small differences in the drying kinetics of mortars cast with and without SRA, which, if reproduced, would allow a simpler comparison between changes in nonlinear elasticity mainly due to saturation degree decrease and changes mainly due to associated cracking [WLRS08].

Finally, measurements of nonlinear elastic moduli evolution during drying in specimens with and without SRA may also allow to better assess how much cracking is reduced by the usage of SRA, reduction which is one of the main purpose for using such admixtures in cement-based materials. Typically, the reduction in cracking is simply inferred from the reduction in linear or volumetric shrinkage, even though only complex and not known non-linear relationships exists between shrinkage and cracking metrics.
3 Methods and experimental setup

3.1 SIngle MOde linear Resonance Ultrasound Spectroscopy (SIMORUS)

Resonance Ultrasound Spectroscopy is a nondestructive acoustic testing method which was developed by Anderson, Soga and Schreiber in 1970 at Columbia University. [May96] Since then, the technique has been further developed and applied to different scientific fields. The idea of determining the dynamic elastic moduli from ultrasound resonance frequencies was convincing and easily appliable.



FIG. 3 Locations of Driver (or Impact) and Needle Pickup (or Accelerometer)

Figure 8: Excitation of transverse, longitudinal and torsional mode according to ASTM C215-08 [AST08]

Linear RUS is based on theoretical assumptions i.e., that the examined body is a homogeneous, elastically linear and isotropic, well or rather regularly shaped solid. These assumptions are mathematically summarised by the combination of three physical basic laws which are used to indirectly estimate the elastic constants appearing in them as unknown parameters and arguments of model functions which provide the resonance frequencies of the specimen. Such functions allow solving the direct problem: if the elastic constants and the density of the mentioned idealised specimen are known, the functions allow computing the resonance frequencies. The solution of the corresponding inverse problem consists in looking for optimal estimates of the elastic constants such as the computed resonance frequencies are as close as possible to the measured frequencies. The three essential physical laws used for describing the elastodynamics problem at the basis of the mathematical formulation of the problem are Hook's law, Newton's second law and the definition of Lagrangian density function of the specimen. By the Rayleigh-Ritz method, a solution is calculated approximately so that the elastodynamics variational problem can be simplified and converted into as algebraic pseudo-eigenvalue problem which is solvable by numerical methods. [May96] [ZRAS04]

The general linear RUS considers the case of a measured resonance frequency spectrum containing peaks, i.e., resonance frequencies, associated to any possible type and order of vibration eigenmode. SIMORUS consists in performing one or more resonance frequency measurements designed to excite preferentially one specific type of vibration eigenmode. Based upon approximations about the geometry and the coupling degree between longitudinal and shear deformations, direct, analytical equations can then be derived from the basic equations of linear elastodynamics which directly relate one type of elastic constant or modulus, e.g., the Young's modulus of an elongated and thin bar, with one specific type of resonance frequency, e.g., the 1st longitudinal resonance frequency.

For SIMORUS, the experimental set up is essential in order to preferentially, if not exclusively, excitate the planned eigenmode. Three main types of eigenmodes are normally used to measure the Young's modulus and the shear modulus. In the American standard ASTM C215-08 [AST08], the measurement setup is explained (see Fig.8) and the equations relating the Young's modulus with the 1st longitudinal resonance frequency, the same modulus with the 1st flexural resonance frequencies and the shear modulus with the 1st torsional resonance frequency are presented. One of the main obstacles in the experimental implementation of SIMORUS in the first place is to identify the resonance frequency associated with the eigenmode of interest in the measured resonance spectrum. Even when the specimen has size, geometry and physical properties that largely satisfy all of the approximate conditions required by the method, e.g., for the preferential excitation of longitudinal eigenmodes the specimen needs to be an elongated thin homogeneous rod, the couplings between longitudinal and shear deformations and sources of experimental errors lead to complicated spectra where not all the peaks are associated only to longitudinal modes and some of the peaks may be even not associated to eigenmodes at all but may be due to spurious factors or measurement noise. By knowing the spatial patterns of the standing waves creating the different eigenmodes, the classification is possible by e.g., exciting sinusoidally the specimen at a unique frequency where a peak is located in the spectrum and by looking for the characteristic nodes of the relevant eigenmode or by producing Lissajou figures which form a 45° rotated ellipse at the corresponding eigenfrequency. The latter method simply consists in plotting interactively during the measurement the excitation sinusoidal signal on the horizontal axis and the measured output one, e.g., the vibration displacement, on the vertical one. In resonance conditions, a specific phase difference exists between the input oscillation and the output, resonance-produced one, such that a particular trajectory is drawn by the moving point on the screen of, e.g., an oscilloscope.

In figure 9 the experimental setup of SIMORUS measurements performed in this Thesis work is shown by a block diagram. The parameters such as the driving amplitude, vertical resolution of the digital acquisition card and of the period waveform function generator and frequency step were set in the Resonance Inspection Techniques and Analysis (RITA) software developed at the Los Alamon National Laboratory, National Nuclear Security Administration, Dept. of Energy, USA [PUB⁺14]. This software controls each step of the measurement, communicating via a National Instruments (NI) chassis (NI PXIe 1073 by National Instruments with the



Figure 9: Technical setup of SIMORUS

periodic waveform function generator (a NI PXIe 5406 card) and the digital acquisiton card (NI PXIe 5122, 14 bit, 200 MHz max. sampling frequency)). Before the specimen is excited, the generator sends the excitation signal to a fixed gain amplifier (High-Voltage Amplifier, Model 2350 by TEGAM) which multiplies the signal by a factor of 50 limited by 400 Vpp maximum as output. By the electrical input through the transducer, the specimen in free boundary conditions starts to oscillate when a eigenmode occurs. These small movements are measured by laser vibrometer which sends the information back to the computer via generator. Whereby, the software draws simultaneously a spectre.

The SIMORUS measurements have been implemented according to the ASTM C215-08 standard, with the configuration for preferential excitation of longitudinal vibration eigenmodes (Fig. 8b). As excitation source a pin-like piezoelectric transducer (Valpey Fisher VP-1063, 1mm diameter, longitudinal wave transducer with 2.2 MHz resonance frequency) has been used, put in contact with the specimen via a bar holding the transducer itself and applying a torque to the bar itself in order to guarantee a stable contact. Both the specimen surface and the transducer were covered with grease in order to improve the contact. The specimen was suspended in air, inside a sealed glove box with controlled relative humidity, hold by two Naylon thin threads located close to the mid of the cylinder, where a node is expected in the case of vibration at the 1st longitudinal resonance frequency. As a receiver, the laser beam of a velocity vibrometer was shun on the surface opposite to the one where the source was applied, in order to measure the component of the velocity vector field oriented along the longitudinal axis of the cylinder. The laser vibrometer as a receiver guaranteed a non-contact measurement of the vibration signal at the location on the specimen where the spatial pattern has maximum amplitude in correspondence of the 1st longitudinal eigenmode. The pin-like transducer and the holding by hanging with thin Nylon threads in the vicinity of the node guaranteed to approach as much as possible the (stress) free boundary conditions necessary for increasing the success in preferentially exciting longitudinal

eigenmodes. Each measurement consisted in applying a sinusoidal signal with constant amplitude and frequency to the source transducer, waiting a time $\Delta t_{ring-up} = 15ms$ until the achievement of a steady state, recording the signal during a successive time interval $\Delta t_{acq} = 30ms$ and computing by Fourier analysis the amplitude of the signal component at the excitation frequency, which was plotted then, during the running measurement, on a plane with the excitation frequency on the horizontal axis and the vibration amplitude (in Volts) on the vertical one. This procedure was repeated successively and automatically by increasing the excitation frequency within a certain interval $[f_{min}; f_{max}]$ and by a step of $\Delta f = 100Hz$. The vibration amplitude voltage was then converted, in post-processing of the data, into vibration velocity amplitude by the laser vibrometer dynamic range conversion factor Λ , expressed in $mm/(s\dot{V})$ and set differently for the stone and the mortar specimens, $25mm/(s \cdot V)$ and $125mm/(s \cdot V)$.

By means of SIMORUS, the dynamic elastic modulus was determined through measurements in the longitudinal mode and the shear modulus which has been calculated through a numerical combination of results of the longitudinal and transverse mode based on ASTM C215-08 [AST08]. The first torsional eigenmode could not be excited unamiguously why a direct calculation according to the standard ASTM C215-08 [AST08] was not feasable.

3.2 SIngle MOde Nonlinear Resonance Ultrasound Spectroscopy (SIMONRUS)

SIMONRUS is implementation-wise comparably similar to the linear one. The only but key difference consists in the fact that, in SIMONRUS, the frequency sweep is repeated N times, at each time increasing monotonically, in its standard implementation, the amplitude of the excitation sinusoidal voltage signal applied to the source transducer such that the correspondingly excited standing waves which put the specimen in resonance have increasing dynamic strain amplitude $\delta\epsilon$. By increasing the driving amplitudes the resonance frequency of a specific vibration eigenmode changes, specifically for most materials, it decreases. As mentioned in Section 2.2.1, cement-based materials and many stones, as well as other consolidated granular materials as ceramics, many polycrystalline materials and, in general, micro-cracked materials, exhbits a linear scaling between the relative change in the resonance frequency, $\frac{\Delta f_{i,0}}{f_0}$, and the dynamic strain amplitude (average over one cycle of the strain wavefield), $\Delta \epsilon_i$, where the index i = 1, 2, ..., N simply enumerates the increasing excitation amplitude values, which correspond to increasing $\Delta \epsilon$ values, f_0 is the resonance frequency at the first and the lowest of the excitation amplitudes, which must be small enough not to induce any nonlinear elastic response, and $\Delta f_{i,0}$ indicates the difference between the resonance frequency in correspondence of the *i*-th excitation amplitude and f_0 . Such linear scaling between those two variables is not predicted by the classical, atomic-scale theory of nonlinear elasticity but only by its mesoscopic extension, which considers features as cracks and grain boundaries of polycrystalline materials as sources of the observed macroscopic nonlinear elastic beahvior. As reported in Section 2.2.1, the direct proportionality constant between the two variables, called α , is a parameter directly appearing in the (1D) mesoscopic nonlinear stress-strain EoS (see Eq. 2.39), called a (1D) nonlinear (mesoscopic) elastic modulus. As nonlinearity grows, the peak of each driving amplitude is shifted in comparison to the next lower or higher amplitude. The following equation can be expressed as [EPB+15]

$$\frac{\Delta f_{i,0}}{f_0} = \alpha \Delta \epsilon_i \quad \forall i = 1, 2, ..., N$$
(3.1)

is a key relationship between the two mentioned variables which are typically measured in a SIMONRUS measurement. [EPB⁺15] [JS05] [CKKJ11] The technical setup (compare fig. 10) differs in one main point: As



Figure 10: Technical setup of SIMONRUS

transducer, a larger sensor is chosen creating fixed boundary conditions on one side of the specimen. Thus, the identification of the modes is more complicated due to the added weight on the sample but the results contain more information than the linear ones.

By applying multiple driving amplitudes to a solid, the material corresponds in scale of its internal damage and its inhomogenities. In this work, the specimens have been oscillated by amplitudes between 1Vpp and 56Vpp to avoid conditioning. Higher amplitudes address to the nonlinear elastic behaviour of a solid, so that the peak will shift with increasing amplitude, if a certain nonlinearity is present (see Fig.11). In general, SIMONRUS spectra are detected by driving the amplitudes up&down, by means of going from the lowest frequency of the interval to the highest and the otherway back (from high to low). Haupert et al. [HRR⁺11] have developed a protocol to correct or rather erase the influence of temperature changes during the measurement. Since



Figure 11: Spectrum of SIMONRUS measurement

the process of measuring can take multiple minutes (depending on the input values), modifications in temperature manipulate the results of amplitude shift. By detecting the ground amplitude, e.g. 1Vpp (see thicker line at lowest amplitude Fig.11), after every drive amplitude (e.g. 6Vpp, 11Vpp, ..., 60 Vpp, ...), the amplitude shift always refers to a current state of the specimen by respecting temperature changes.

3.3 Materials and mixtures

For running the experiment, two different types of mortars and a sandstone have been chosen. The mortars are similar regarding their mixture, besides the usage of a shrinkage reduction admixture (SRA) (compare table 1). The specimen preparation and the experimental campaign are described in the following section. The Vosges sandstone is catagorised as a red sandstone, whose colour indicates a significant content of iron oxides. This type of sandstone can exhibit a porosity up to 25 %. As the name reveals, the sandstone was exploited in the Vosges mountaines in eastern France, close to the German border [Okr14].

Material	Density	Mass
	(kg/dm^3)	(kg/m^3)
drying_oSRA		
w/c-ratio = 0.5		
Jura Cement OPC CEM I 42,5 N	3.16	500
Sand (volume 50 %)	2.68	1169
Tapwater	1.00	250
drying_SRA		
w/c ratio = 0.5		
Jura Cement OPC CEM I 42,5 N	3.16	500
Sand (volume 50 %)	2.68	1195.5
Tabwater	1.00	243
Sika Control-60: Shrinkage Reducing Admixture (SRA)	1.01	10

Table 1: Mixture of both mortar types

3.4 Standards, directives and other characterisation methods

Sorption isotherms

According to DIN EN ISO 12571 [DIN00b], the sorption isotherms of the mortar mixtures and of the sandstone were measured. Based on the standard, the method using desiccators was chosen to perform the testing. For the performance, six atmospheres were specified: 97% RH, 75% RH, 60% RH, 43% RH, 23% RH and 14% RH. The specimen were stored at $20\pm1^{\circ}$ C whereby the different relative humidity values in the desiccators were created by water-based solutions of potassium sulfate (97% RH), sodium chloride (75% RH), sodium bromide (60% RH), potassium carbonate (43% RH), potassium acetate (23% RH) and potassium hydroxide (14% RH). Additionally, the sandstone's sorption isotherms were measured by Dynamic Vapor Sorption (DVS), as a pree-valuation to evaluate the time the drying process takes to achieve euqilibrium at one realtive humidity value. A DVS lab instrument by Porotec, model no VTI-SA Q5000, was used whereat the input parameters were set to a drying temperature of 40°C and to relative humidity values in increasing/decreasing steps of 10% . The equilibrium criterium was defined as a mass constancy of 0.001 m.% for 10 minutes. The stone specimen was

kept 12 hours and the mortar specimens for 7 days in the DVS machine. To perform one adsorption and one desorption cycle, for an informative and full sorption isotherm curve. Based on the vapour diffusivity of each material, the testing time differed widely.

Porosity and pore size distribution

The porosity as well as the pore size distribution of the sandstone and the different mortars were determined by means of Mercury Intrusion Porosimetry (MIP, machine: Pascal 140 Series by ThermoFinnigan). MIP is an often utilised and comparably accurate method to evaluate the porosity and the pore size distribution. This method is based on the property of mercury as a non-wetting liquid with a high surface tension. During a MIP measurement, the liquid mercury enters large pores and capillary ones (i.e., nano-scale pores, in cement-based materials) under the action of an increasing hydrostatic pressure applied to the specimen + mercury volume. The pore size and the required pressure permeating the pores of the given size correlate, according to the Washburn equation similar to Eq. 2.44, derive from the Young-Laplace equation for the simplistic case of cylindrical pores described as capillaries:

$$P = \frac{-4\gamma\cos\theta}{d} \tag{3.2}$$

where P describes the pressure, γ the surface tension of the liquid, θ the contact angle of the liquid and d the diameter of the capillary [Gie06], [AWL99]. The model, on which MIP is founded, assumes that every pore has a cylindrical shape. In reality, the complexity of different pores and their networks or, rather, connections, are one of the most difficult structures to determine. Therefore, the model entails some features which increase the error in the results. Furthermore, the limitations of MIP have to be acknowledged to illustrate possible errors: concerning the ink-bottle theory [Gie06], [KLL09], a miscalculation of the pore size occurs because of the small entrance of the pore compared to its actual size or rather shape. Moreover, the phenomenon that some mercury remains in the specimen after depressurisation is probably explained by contact angle hysteresis, although Giesche [Gie06] suggested the theory that the phenomenon of remaining mercury is not clarified yet and not caused by contact angle hysteresis. Besides these features, the method is limited by the maximum pressure and by the size of the specimen regarding the largest measurable pore. In addition, the results can be biased by the stability or compressibility of a material, e.g., a loosely packed powder could be compacted by the high confining hydrostatic pressure or an elastic structure could be deformed in complicated ways. [Gie06], [KLL09], [AWL99].

In addition to MIP measurements, specimens were saturated with water under "vacuum" (20 mbar) and the bulk porosity measured based upon measurements of mass before and after water saturation, according to the standard ASTM C 642 [AST04]. In consideration of the different methods for measuring the bulk porosity, the vacuum saturation-based one was chosen as different articles in the literature concluded that it is the most accurate one [SMJ11], [SH05].

The porosity and its size distribution of a material reveal on the one hand possible occurring forces during the evaporative drying, corresponding damages and on the other hand, the time to reach equilibrium.

3.5 Experimental campaign

Within the scope of this Master Thesis, specimens of a sandstone and of two different mortars (see Section 3.3) have been tested at various decreasing relative humidity values and conditions. The experimental campaign with of the mortar specimens is shown in Figure 12. The sandstone specimens were subjected to identical measurements as the mortars ones. What distinguished the experimental campaign with sandstone and mortars specimens was the way to induce drying: both types of specimens were stored in environments at different, controlled RH values. Such values were constant during the overall Master Thesis work for the mortars, because of the large time scale needed to achieve equilibrium between the internal and external RH. On the contrary, the external, drying-driving RH values decreases in time for the sandstone specimens, because they could achieve the same type of equilibrium at the time scale of a few days/weeks, such that during the duration of the work it was possible to bring the internal RH of such specimens at distinct (decreasing) values in order to continuously dry them. One important feature of the performed experimental campaign, which entails the obtained results of uniqueness compared with what so far published in the literature, is the execution of the SIMORUS and SIMONRUS measurements inside a glove box with RH equal to that of the dessicators where a given type of specimen was left in between measurements times, for drying. This feature allowed minimizing water content changes during such measurements, thus minimizing any perturbation of the drying process itself. Regarding the external RH values for driving the drying, their ranges included values already used, e.g., for the sandstone specimens, already in other studies reported in the literature [VCJZ02], [PGM10], [EPB+15].

Preparation and testing of fresh mortar and hardening mortar

The mortars specimes were mixed according to the mixing regimens of the DIN EN 206-1 [DIN00a] (see Table 2). After mixing, the slurry was cast in cubic moulds (150 x 150 x 150 cm³). By means of a vibrating table, such cubes were compacted for 90 secounds. The fresh mortars were characterised by a slump test (DIN EN 1015 - Part 3 [DIN99, part 3]), by fresh mortar raw density (DIN EN 1015 - Part 6 [DIN99, part

Duration	Action
30 sec	mixing of cement and sand
30 sec	adding water (and SRA)
90 sec	mixing

Table 2: Mixing regimen of the mortars according to DINEN 206-1 [DIN00a]

6]) and by air void content test (DIN EN 1015 - Part 7 [DIN99, part 7]). Afterwards, the cubes were stored for 24 h at 20°C and 90 % RH covered with a foil. After the removal of the framework, the specimens were submerged in water for curing until the 42nd day after mixing (see Fig. 12). At the 7th day, the cubes were cored to cylinders with a diameter of 28 mm and a length of 150 mm. Moreover, cylinders for compressiv strength testing (diameter = 50 mm and length = 50 mm) and static Young's modulus determination (diameter = 50 mm, length = 150 mm) were also cored.

The actual experimental campaign started at the 42nd day by measuring the compressive strength, the internal relative humidity, via internal removable sensors, the length of dedicated specimens (equipped with reference with bolts, to be sure to measure the length along the cylinders' symmetry axes always at the same positions)



Figure 12: Chronological presentation of the experimental campaign; AC: autogeneous conditions, RH: relative humidity

and their mass and the linear and nonlinear elastic moduli via SIMO(N)RUS. By SIMORUS, the longitudinal and transverse mode were measured through different setup according to ASTM C215-08 [AST08]. In between two measurement sessions, the specimens were stored in desiccators at the distinct relative humidity values for two sets of specimens, one set drying at 75% RH and the other at 43% RH. 6 additional specimens were stored in plastic, sealed bags put in plastic boxes located in a climatic chamber at 90% RH and 21°C. Such specimens were thus subjected to distinct boundary conditions, likely leading only to autogeneous drying. These specimens were used as a sort of "reference" specimens not subjected to evaporative (environmental) drying.

To improve the statistical robustness of this experimental campaign, 3 specimens of each material and each different mixture (5*3 specimens) were tested by each method, except for DVS and MIP, just one specimen was used.

Preparation of and measurements on the sandstone

The sandstone specimens were also cored (diameter = 28 mm) from a meter-scale slab and cut to a length of 150 mm. Additional cylinders were stored at 21 $^{\circ}$ C and 90 % RH in plastic bags until preliminary character-

isation measurements were performed on them. Those measurements probed such material properties such as the sorption isotherms and the porosity by MIP and by vacuum saturation.

By starting the experimental campaign (see fig. 12), the sandstone subjected to environmental evaporative drying specimens were stored in a desiccator until they reached their equilibrium at the initial relative humidity of 98 % RH. Afterwards, they were subjected to the same set of measurements as the mortars specimens were (see Fig. 12). Concluded the measurement session, the specimens were stored in a new dessicator at a lower RH and let there till they reached internal relative humidity approximately equal with the external one, when they were subjected again to the set of measurements. The procedure continued until a final external RH value of about 14%. As for the measurement campaign with the mortars, 6 sandstone cylinders were stored in sealed plastic bags located in the same climatic chamber at 90% RH and 21 °C and measured upon at the same times as the other specimens. Such specimens were used as well as "reference" specimens not subjected to drying (shrinkage).

4 Results and discussion

4.1 Examination of the Vosges sandstone

4.1.1 Porosity and sorption isotherms

The pore size distribution or rather the porosity itself impact the evaporative behaviour significantly. The Vosges sandstone is a sedimentary rock with a fine size of grains and a porositiy of about 20 % [VCJZ02] [ESF17]. In this work, the Vosges sandstone was analysed concerning its porosity by vacuum saturation and MIP. In Figure 13, the results of those measurements are presented. At first, a difference between both porosity



Figure 13: Porosity of Vosges sandstone, results by MIP and vacuum saturation

values measured by the two distinct methods is recognisable whereby a porosity of 18.74% was determined by vacuum saturation and 16% by MIP. On the one hand, the accuracy of MIP for porous materials as sandstone, with a rather large fraction of large (tens/hundreds of microns) pores and a rather narrow-band pore size distribution, compared with cement-based materials, thus more limited influence of the ink-bottle effect, is higher than the one of vacuum water saturation. Even though vacuum saturation is typically considered as the most exact porosity measurement method among the saturation techniques [SMJ11], because of small errors associated with resolution of the used balance, additional biasing influences related with the laboratory worker and the climatic conditions have likely affected the accuracy of the porosity measurements of this stone. On the other hand, the value of 18.74% obtained by vacuum water saturation approaches the values in the literature (compare with [VCJZ02] [ESF17]). Assuming the MIP result as the most reliable one, the obtained lower value compared with what reported in the literature can be a hint that the examined sandstone may be a more compact Vosges sandstone. Hence, there could be an influence of the level of (geolocial scale) compression of the chosen sandstone on the MIP result : under applied pressure the stone can be densified,

which leads to lower porosity values [ZJR97].

In regard to the pore size distribution (see Fig. 13, rigth inset), most of the pores are concentrated in pore radius ranges between 6 000 and 25 000 nm. Therefore, it can be concluded that the distribution is concentrated within a rather narrow band of large pore size, where "large" has to be compared with the nm scale. This concentration in a narrow band of large, micron scale, pore size implies that the contained water in the material can be removed by evaporative drying rather fast compared with what possible in the mortars (see Figs. 31 - 32 and 57 - 58 for the mortars specimens) and the stresses and strains caused by drying shrinkage should lead to less cracking because of smaller capillary pressure (see Section 2.3.2). Moreover, the curves in Figure 13 show that some of intruded mercury was kept in the specimen during the extrusion part of the measurement: there is a large difference between the extrusion curve of the first intrusion-extrusion cycle and the at of the second cycle.



Figure 14: Sorption isotherm of Vosges sandstone, dried at 40°C

The sandstone was initially dried at 40°C and measured by DVS (increasing/decreasing relative humidity in 10% steps from 0% to 95% RH and then back to 0% RH). Figure 14 shows an almost linear rise in (gravimetric) water content until 60% RH and afterwards an exponantial increase until 95% RH. During the desorption, a divergent development is observable. The curve declines more rapidly in an interval between 95% RH and 60% RH. Thereby, hysteric effects are revealed which may indicate a "stronger" nonlinear elastic behaviour in that relative humidity range.

4.1.2 Consideration of drying shrinkage parameters

For the characterisation of the drying shrinkage of the specimens, three typically assessed parameters have been measured and calculated. The drying rate is the first one, defined $\tilde{e}(t_i) = -\frac{1}{\rho S} \frac{m(t_{i+1}) - m(t_{i-1})}{\Delta t}$. Here \tilde{e} represents the not-normalised drying rate (no normalisation of it by the environmental drying rate, computed in the same way but for a column of water), t_i a time point during the experimental campaign. ρ the volumetric

mass density and *S* the area of the boundary surface through which water vapour can escape. The first measurement of the mass was performed after 42 days at 98% RH (the time axis was synchronised with the hardening of concrete, therefore 42d were used as the starting temporal point for the measurement campaign for the sandstone specimens as well). Concerning the definition of the drying rate (see equation), the curve starts though at day 49 and ends at day 70 and includes four values whereas all the other measurements on the specimens have been performed after they reached equilibrium at six different relative humidity values, thus for longer than 70 days from the specimen coring. An unambiguous development of the curves is recognisable



Figure 15: Drying rate of Vosges sandstone at relative humidity values between 98% RH and 14% RH (AC - autogeneous conditions at 90%RH)

Figure 16: Longitudinal shrinkage of Vosges sandstone at relative humidity values between 98% RH and 14% RH (AC - autogeneous conditions at 90% RH)

in Figure 15. At high relative humidity values, e.g. between 98 and 60%, the sandstone is driven to loose an higher amount of water, compared to lower relative humidity values, e.g., 40-14% (see Fig. 15). The trend agrees well with the results of the soprtion isotherm (compare Fig. 14). After 60 days (RH of 43%), the drying decelerated significantly and seemed to start an almost constant development. A similar trend but for water gain instead of loss can be observed for the specimens in autogeneous conditions. However, the drying trend is typical of a rock in the falling rate period (see Section 2.3.2).

When the shrinkage of the Vosges sandstone is also considered, rather small values (compared with what achieved by the mortar specimens, even at higher external RH values, see Fig. 83 for the comparison) are recognisable (Fig. 16). From 98%RH to 43%RH, the curve decreases almost linearly to a shrinkage value of $-7*10^{-5}$ cm/m, while the specimens expanded slightly between 43% and 23%RH and continued thereafter almost constantly. The specimens in autogeneous conditions exhibited almost no shrinkage at all, as well as no expansion except for the last point of time. The corresponding drying rate curve (Fig. 15) indicated a gain in water content, especially at the beginning of the experimental campaign. Despite the clay content characterising this type of sandstone and the hygroscopic properties of these clays, the water gain did not lead to significant, macroscopic scale swelling of the specimens.

The last measured parameter in this context is the internal relative humidity. In Figure 17, the internal relative humidity is plotted against the external one, whereby the red line indicates a linear straight line (y=x). Most of the values follow the suggested fit except at 75% and 60% external RH. The internal value at 60% external RH

is lower (ca. 54% RH) than the following values at lower RH values. The utilised transducer for the internal RH measurements is quite dependent on a correct calibration at each RH level. Thus, it could be that the transducers got calibrated to a slightly lower RH for the value of 60% external RH. Furthermore, the specimens could loose some water also during these measurements (which were not performed, as the SIMO(N)RUS ones inside a glove box with controlled environmental RH) so the result differs from the expected value. However, the trend differentiates the most from the linear fit at 75% external RH. Due to the narrow band and homogeneous distribution of large pores and the small amount of pores < 100nm, the sandstone should show, after reached equilibrium, the same internal relative humidty value as the external one. Therefore, also this divergence can be explained by measurement transducer calibration biases. Despite these divergences from the expected linear trend, the used Vosges sandstone is, as expected, characterised by a rapid drying leading, within a few days/weeks to almost perfect equilibrium between the external, drying-driving RH and the internal one. As explained in Sections 2.3.2 and 4.1.1, the fast achievement of equilibrium is due to the prevalence of rather larger pores, when compared with the pore size range and size distribution of cement-based materials.



Figure 17: Internal relative humidity development during drying of Vosges sandstone

4.1.3 Results of resonant ultrasound spectroscopies

The elastic behaviour of the sandstone was examined by SIMO(N)RUS during the evaporative drying at different relative humiditiy values. Sandstones, especially clay containing ones, are sensitive to changes in water content [ZJR97] [VCJZ02]. A "stiffening", i.e., an increase in linear elastic moduli is typically observable with decreasing water saturation degree, in this experimental campaign obtained with decreasing internal relative humidity. As Figure 19 reveals, the (dynamic) linear Young's modulus of the solid increases with decreasing relative humidity. On the one hand, the clay contained in this type of sandstone tends to swell in correspondence of water increase. It should be expected that a swelling should result in a "softening" of those parts in the solid, i.e., a diminution in (dynamic) linear elastic modulus. Thus, a decrease in water saturation degree should be accompanied by a shrinkage of such clay minerals and their consequent stiffening, signaled by an increase of their linear elastic moduli. On the other hand, a decrease in water saturation degree means an increase in capillary pressure as well and disjoining pressure, leading to an increase in local stresses. When



Figure 18: Resonance frequencies of the first longitudinal vibration eigenmode at different relative humidity values (AC - autogeneous conditions at 90% RH)

Figure 19: Dynamic Young's modulus of Vosges sandstone at desorption (AC - autogeneous conditions at 90%RH)

the dynamic linear elastic modulus values are compared with results reported in other articles different values can be found. For example, different sandstones, including a type of Vosges sandstone called Meule, have been examined by Van Den Abeele [VCJZ02] concerning the influence of water saturation degree. In this article, dynamic Young's modulus values in a range of 3 to 9 GPa are reported, measured with SIMORUS as well but with excitation at 550-950 Hz. In contrast, the values reported in this Master Thesis have been measured at frequencies between 8600 Hz and 10100 Hz (see Fig.18). Considering the equation relating approximately the linear Young modulus Y and the 1st longitudinal resonance frequency, $Y = 5.093(L/d^2)Mn^2$ [AST08], where L is the length of the cylinder, d the diameter, M the mass and n the 1st longitudinal resonance frequency, the difference is reasonable, considering the dependence of the longitudinal wave phase velocity from the frequency of the standing waves and from the mass density.

At the beginning of the experimental campaign, specimens have been tested concerning their compressive strength and static elastic modulus in order to have additional information about the mechanical properties of such sandstone. The measured compressive strength was 57 MPa, whereby it can be categorised in the high range of values of this mechanical property, according to what reported in the literature [BDR00]. Moreover, the static elastic modulus was determined as 17.3 GPa at a relative humidity of 98% RH.

The same specimen have been also measured by nonlinear RUS, SIMONRUS. As expected and already reported in the literature [VCJZ02], due to the high sensitivity of SIMONRUS to changes in the poromechanical properties, changes in the nonlinear elastic behaviour due to of environmental conditions, like temperature and relative humidity, are visible in the results. First of all, it can be recognised, on the one side, that the

vibration amplitude increases with diminishing RH, a trend which can be due to both nonlinear elastic properties and to linear poromechanical processes (smaller water content means less viscous attenuation of the standing waves by the water in the pore space). On the other side, the overall range of resonance frequency values peak moves into a higher frequency range with reducing RH. This is the result of the stiffening with decreasing saturation degree already discussed in relation with the dynamic linear Young's modulus dependence on it (Fig. 19). At this point, it has to be mentioned that the spectrum of specimen 3 in Figure 20(c) is not shown because of measurement problems occurred only in that case.

Figures 20 and 21 clearly show, from a qualitative point of view, the typical dependence of a resonance frequency from the excitation amplitude, thus from the amplitude of the strains induced into the specimen. With increasing excitation amplitude, thus strain and consequently also vibration velocity amplitude, plotted on the vertical axis in those figures, the resonance frequency decreases, the resonance curve becomes less symmetrical around the resonance frequency, at the point of getting distorted in correspondence of the largest excitation amplitude, all of which are typically effects predicted by nonlinear elasticity theories. One specimen has been measured multiple times at 23%RH to evaluate the potential influence of the quality of the contact between the source transducer. Poor contact and consequent coupling between the two materials can lead to nonlinear effects as well, unrelated with bulk nonlinear elastic properties of the investigated specimens. For this purpose, the chosen specimen was uncoupled from the transducer after each of theses test measurement and re-glued. The results are presented in Figure 22. At first glance, the spectra seem to be satisfactorily similar. Some small difference is recognisable, like the variation in the resonance frequency range (compare e.g. insets (a) and (b)) and variation in frequency shifts. The measurement are sequentially arranged so that by time repetition a decrease in in resonance frequency shift is noticable, except specimen (e) (see Fig. 22). This phenomenon shows that slight changes in spectra are caused by the un- and re-glueing of the transducer. For example, residues of the used glueing/coupling material (phenyl silicilate) could remain on the specimen whereby the coupling of the sandstone with the transducer is slightly decreased. Therefore, the sensitivity of the method can diminish which could be the explanation for a slight decrease in the linear resonance frequency shift with repeated measurement on the same exact specimen. Moreover, the repeated excitation of the same specimen by repeated SIMONRUS measurement on it can cause changes in the solid so that a variation in peak frequency can be possible. In this case, a softening would take place concerning the reduction in resonance frequency by repetition (see Fig. 22). Such conditioning was observed not to be too large, even though still slightly occurring, during a single execution of the SIMONRUS measurement on a specimen, thus the use of the Haupert's protocol to remove its influence on the quantitative assessment of the nonlinear elastic response of the specimens.

To provide more informing data, the average value +/- standard deviation, both computed over the results from the three specimens, of the absolute value of the relative change in resonance frequency, computed according to the Haupert method, has been plotted as a function of the respective average value (+/- standard deviation) of the vibration velocity amplitude, for each external RH values (Fig. 23). As explained in Section 3.2, either a linear or a quadratic scaling relation should be expected between the variable plotted on the vertical axis of Fig. 23 and the variable plotted on the horizontal one, the power law exponent depending upon the "class" of nonlinear elastic behaviour. Thus, the experimental data shown in Fig. 23 should be fitted by an equation of the type $y = a * x^b$.



Figure 21: SIMONRUS spectra of Vosges sandstone at relative humidity values between 43% and 14%; vibration velocity amplitude [0 ; 2.5] mm/s; frequency [4800 ; 6000] Hz

Figure 20: SIMONRUS spectra of Vosges sandstone at relative humidity values between 98% and 60%; vibration velocity amplitude [0; 2.5] mm/s; frequency [4800 ; 6000] Hz



Figure 22: SIMONRUS spectra of the same specimen of Vosges sandstone at 23%RH - repetition of measurements on specimen 1; vibration velocity amplitude [0; 2.5] mm/s; frequency [4800; 6000] Hz.

The parameter *a* expresses the nonlinearity strength, *x* the vibration strain amplitude, *y* the absolute value of the relative change in resonance frequency and *b* the nonlinear elasticity class-dependent power law exponent. By means of *b*, it can be determined which theory is the most suitable one for describing the examined material. If b = 1 (in theory or close to it in reality), the solid can be described by mesoscopic elasticity theory. If b = 2 (or close to it in real data), for example, the classical theory is the best approach to choose. Figure 24 shows the same data of Fig. 23 (only the markers, representing the average values) but in a double logarithmic scales. With such plot, the meaningfulness of describing (thus fitting) the data according to the power law model $y = a * x^b$ becomes qualitatively clear: log(y) varies linearly with log(x) and indeed the average values seems to be qualitatively well describable by such a relationship. Figures 23 and 24 clearly show that the decrease in RH led to a systematic decrease in achievable relative changes in resonance frequency. The data shown in the log-log plot in Fig. 24 tend to align themselves along lines which have rather similar slope, which points to rather similar values of the parameter *b*, i.e., same class of nonlinear elastic behavior, but which have decreasing value of the intercept with the vertical axis, i.e., decreasing a value, or nonlinearity strength.

First of all, here are two outstanding points which catch the eye at first glance in Figure 23: in correspondence of the second largest amplitude value at 23%RH, which can be considered as and outlier concerning the trend exhibited by the rest of the data at that RH and the significant scatter of the data (very large error bar);





Figure 23: Absolute value of the relative resonance frequency change, $|(\frac{\Delta f_{i,0}}{f_{i,0}}|)$, versus the resonance vibration velocity amplitude, V_i , for the distinct excitation amplitudes A_i , $\forall i = 1, ..., N$, of Vosges sandstone, in linear scales and with error bars, at relative humidity values between 14% and 98%RH

Figure 24: Absolute value of the relative resonance frequency change, $|(\frac{\Delta f_{i,0}}{f_{i,0}}|)$, versus the resonance vibration velocity amplitude, V_i , for the distinct excitation amplitudes A_i , $\forall i = 1, ..., N$, of Vosges sandstone, in double-logarithmic scales, showing only average values, at relative humidity values between 14% and 98%RH

in correspondence of the largest amplitude value at 75%RH. In the latter case, the large relative change in resonance frequency and the large error bars may this beginning of an hint at a strong starting conditioning effect.

Despite these two values, when the complete trend for each RH dataset is considered (see Fig. 24), a clear course is noticeable. The relative frequency shift unequivocally monotonically decreases with decreasing RH. It is striking that the data points towards the lower resonance vibration velocity amplitudes tend to be more scattered around the theoretical power law curves (see Fig. 24 and later on in Fig. 28). This is a typical feature of SIMONRUS measurement results: resonance peaks at smallest excitation amplitudes are more difficult to reliably detect because of higher signal-to-noise ratio of the acquired vibration velocity signal at such amplitudes. Normally, the laser vibrometer acquisition resolution and the analog-to-digital conversion resolution are setup for being able such that at the largest excitation amplitude the corresponding vibration velocity signal does not fall above the maximum value which can be detected and digitized. This has the disadvantage of large bin size for the analog-to-digital conversion, which means lower resolution of small amplitude vibration signals.

The quantitative analysis of the data of Fig. 23 has been performed with the above mentioned fitting, for each RH level. Instead of performing a linear fitting of the log-log data of Fig. 24, which would have led to statistical methodological error, a nonlinear least squares fitting based upon the Levenberg-Marquardt non-linear optimization algorithm [Lev44] [Mar63] has been used directly on the linear scales data as in Fig. 23. Instead of using the average values of Fig. 23, the three corresponding original datasets, for the three distinct specimens, have been fit separately, leading to three distinct values of each best fitting parameter over which to compute average value and standard deviation, the latter used as definition of half error bar. The fitting





Figure 25: Average value (black square markers) +/-1 standard deviation of the *a* best fitting parameter obtained by the power law fitting $y = a * x^b$. The red curve reports, for each RH value, the average value +/- 1 standard deviation of the coefficient of determination R^2 of the power law best fit.

Figure 26: Development of parameter b ($y = a * x^b$) of Vosges sandstone at relative humidity values between 98%RH and 14%RH

was first performed with two free degrees, \boldsymbol{a} and $\boldsymbol{b}.$

In Figure 25, the best fitting nonlinearity "strength" a is shown in depence of the various RH values (black curve). The red curve shows the coefficient of determination R^2 of the fit, which is a goodness-of-fit metric with values between 0 and 1, the closer its value to 1 the more accurate the fit being. When the corresponding best fitting values of the parameter b are considered, in the next Figure (Fig. 26), the values are distributed between 1.1 and 1.55, which show a tendency of the sandstone to be properly described by the mesocopic nonlinear theory, even though, on the other side, the b values are, for each RH level, consistently above 1, as well. Therefore, it may be argued that such sandstone type, although there is a tendency to be more accurately described by the mesoscopic theory. The a values in Fig. 25 depends upon the best fitting b values as well, which vary among the distinct RH values. In order to be able to compare a values across RH levels, the fit has been repeated, for each specimen and for each RH level, by fixing the b value to the average of its average values over the distinct RH levels shown in Fig. 26, such fixed value being 1.33 (see Fig. 27 and 28). By comparing of figures 25 and 27, the variation of the parameter a is reduced and the coefficient of determination is increased. Moreover, the values of nonlinearity strength increased slightly by the second fit. It is clearly observable that with diminishing relative humidity the nonlinearity decreases as well. Due to the clay content in the Vosges sandstone, the clay shrinkage in correspondence of the decrease in RH likely contributed to both the stiffening of the specimens (increase in linear Young's modulus) and to reducing interface features inside the clay minerals themselves. However, given the volumetric amounts of clay minerals (max 5 - 10 vol.%) and the limited macroscopic shrinkage of the specimen, the major contribution to the nonlinearity strength decrease likely came from another source. The capillary pressure rises by the decreasing water content and local micro-cracks are likely closed by an overall compaction-like effect which overcomes the nonlinear elasticity contribution by micro-cracks newly created by the compaction itself.

Such results for the nonlinear strength differ in one trend from the ones in literature, e.g. [VCJZ02] and [JZR⁺04]. The examined Vosges sandstone shows an almost monotonic decrease in nonlinearity with diminishing RH, while a comparable type of sandstones, the Meule, showed a peak in nonlinearity between 15% and 30% water saturation degree, with a significant decrease only from 15% to 0% saturation and a gradual decreasing, increase from 100% to 15% - 30%. This bitrend is in the literature [VCJZ02], [JZR⁺04] explained in terms of different balances in different RH ranges, during drying, between the distinct fluid-solid interactions at play and corresponding balances between activation/deactivation of the microscopic and mesoscopic structural features responsible for the nonlinear mesoscopic elastic behavior, e.g., micro-cracks, grain boundaries and even dislocations inside the polycrystals composing the single mineral grains. Furthermore, a strong local peak in nonlinearity, within a similar interval of water saturation degree, was observed by the same authors for stones with smaller pores.



Figure 27: Average value (black square markers) +/-1 standard deviation of the *a* best fitting parameter obtained by the power law fitting $y = a * x^b$, while *b* fixed at 1.33. The red curve reports, for each RH value, the average value +/- 1 standard deviation of the coefficient of determination R^2 of the power law best fit.

Based on that, the different, only monotonic trend observed in this work's results for parameter a can be explained in terms of the Vosges sandstone, the comparably larger pores and the clay content. The Meule sandstone specimen investigated in [VCJZ02] and in [JZR⁺04] exhibited larger porosity, even larger than the value measured in this work by vacuum water saturation. Larger pore volume fraction means a larger volume fraction of interfacial features of the types mentioned above, considered as sources of the mesoscopic elastic nonlinearity. With a larger volume fraction of such mesoscopic features, the predominance of expansive disjoining pressure over the compressive capillary pressure, at the larger saturation degree values, may have indeed brought to a larger fraction of activated mesoscopic features. In the Vosges sandstone specimens investigated in this Master Thesis a smaller fraction of such features could eventually be activated, leading to a continuous predominance of the compressive capillary pressure over the disjoning pressure, which more likely tends to de-activate the sources of nonlinear elasticity than to activate them. A different pore size distribution and different clay contents could also have led in the Vosges specimens used here to prevalent development of compressive capillary pressure during drying. Finally, recent theoretical research has shown that disjoning pressure develops less likely during drying in a porous material and plays a less significant role in drying shrinkage than capillary pressure [RG17], which calls for a re-interpretation of the local maximum in nonlinearity during drying observed by Van den Abeele et al. [VCJZ02] in terms of some microscopic mechanism at play.

As for the used Vosges sandstone, a decrease in nonlinearity strength with decreasing RH was expected because of the clay content and creation of high capillary pressure values. Moreover, Vosges sandstone is a porous, comparably homogeneous material with large pores so that water can evaporate easily without causing an significant amount of damages, e.g., microcracks. Thereby, the stone stiffens and nonlinearity decreases. These are the reasons why the determined trend was expected in advance and follows a logical scheme. Furthermore, the relative statistical robustness of this work, based on values from three distinct specimens, instead of only one as in [VCJZ02] provides the results here reported a larger degree of reliability.



resonance vibration velocity amplitude [mm/s]

Figure 28: Same plot as in Fig. 24 but with the addition of the power law best fit curves obtained with the second fitting scheme, with the power law exponent b fixed to 1.33 and a as the only fitting parameter. Notice that in log-log scale the best fitting power law curves are perfect lines.

In Figure 28, the log-log scale representation of the data now includes the power law best fitting curves (lines in the log-log plot). As the development of parameter *a* shows, a decreasing trend of the fitted curves is observable with diminishing RH values, whereby the relative frequency shift is reduced, at each resonance vibration velocity amplitude, with progressing drying. The results at 98%RH, especially at the smaller excitation amplitudes, are affected by more scatter because of impairing of the laser vibrometer functioning as small water drops in air distorted and scattered the incident and back-scattered laser beam, thus decreasing the signal-to-noise ratio of the vibration velocity signal. Moreover, the relative frequency shift decreased significantly from 75%RH to 60%RH indicating a higher amount of evaporated water during this drying step compared to other drying steps, which is consistent with the higher values of drying rate at higher RH shown in Fig. 15. In general, the performed power law fit represents the actual raw data sufficiently well and underlines the shown trend of decreasing nonlinear behaviour with reducing RH values.

4.2 Examination of mortars without SRA

Mortar, as a cement-based material, behaves differently during evaporative drying, compared with sandstones, because of different poromechanical properties. Therefore, the process of reaching equilibrium between the external, drying-driving RH and the internal one takes multiple months. As described in Section 3.5, mortar specimens at two distinct RH values have been examined, to monitor the changes in linear and nonlinear elastic properties both before the cited equilibrium is achieved and after it to compare the respective results. In the latter case, the measurements will be performed after the conclusion of this Master Thesis work, given the need of waiting for several months before achieving the equilibrium (especially at 43% external RH). In what follows, the mortars cast without SRA are labeled as "oSRA" specimens and distinguished between specimens dried in a desiccator at 43% RH (oSRA 43RH) and specimens dried in a desiccator at 75% RH (oSRA 75RH).

4.2.1 Quasi-static poromechanical parametes in fresh and hardened mortar

The mortar was cast on two different days, one seperate casting for each RH value. Despite the different mixing days, the fresh mortar properties show similar values (see Fig. 29), except for the porosity. The porosity of the second cast is characterised by a higher result (5.2%) than the first one (3.8%). Both values are acceptable for mortars with a w/c ratio of 0.5. Furthermore, the fresh mortar density as well as the results of slump test are considered as conform to those of a standard mortar.





Figure 29: Fresh mortar properties for the specimens kept at 43%RH and 75%RH.

Figure 30: Mortar properties for the specimens kept at 43%RH and 75%RH, after 42d and 112d after casting.

After 42 and 112 days from casting, further measurements have been performed to evaluate the quasi-static mechanical properties. In Figure 30, the results are presented. Besides the density, the predictable trend is noticeable : the compressive strength as well as the quasi-static Young's modulus grew with time because of the hydration and the stiffening brought by the drying. In the case of these specimens, the drying shrinkage (and the eventually associated cracking) seems not to have had a significant influence on the quasi-static mechanical properties, even though such a conclusion could be validated only by comparing with the values of the corresponding parameters for the specimens stored at autogeneous conditions, measurements for which

have not been performed. Since both at 42 days and at 112 days all the specimens did not yet achieve RH equilibrium, it is possible that the shrinkage and respective cracking was not yet completely maximized, as shown and discussed in Section 4.2.2. The slight decrease in density is explainable by the state of water saturation. At 42 days, the specimens have been tested fully saturated, in contrast, at 112 days, the specimens have been already dried for 70 days and tested at much lower internal RH, approaching the equilibrium for the oSRA 75RH specimens and still decreasing for the oSRA 43RH ones..

Although, the difference in compressive strength of the same mixture at the two distinct casting days is significant, starting with 8 MPa, it decreased to 6 MPa until 112 days. Due to the high heterogeneity of the cement matrix, cementitious materials show in general a certain variation in poromechanical properties, caused typically by cement hydration, construction of the concrete structure, workmanship, etc.

The porosity and pore size distribution of both mortars is considered now, both measured at 42 days from casting, at the beginning of the experimental campaign. When the results by vacuum water saturation and MIP are compared, it is noticeable that the range of porosity values for both mortars are similar, as it should be expected because the oSRA 43RH specimens and the oSRA 75RH ones, at 42 days, did not start yet the drying at distinct environmental RH values. It is recognisable that MIP determined lower porosity values than vacuum saturation (compare Figs. 13, 31 and 32). This phenomenon could be explained by the variation and error of both methods because the values are close to each other, within a narrow range, and it seems that the relative difference between the two results is constantly $2.0\pm0.5\%$ (compare Figs. 13, 31 and 32).

The pore size distribution is for both mortars almost identical. The largest detected pores start at 30μ m and the smallest is found at 1nm. An significant increase from 15 to 65 mm³/g in pore volume exists within the range of 5-30nm. Thereby, the cumulative intruded pore (specific) volume follows a S-curve. The first extrusion indicates that some of the mercury was kept in the specimen based on the ending curve at 33 mm³/g. For this reason, the second cycle do not achieve the same values as the first cycle. However, both cycles presented similar trends, for example both extrusion lines show a shifted increase in pore volume. In extrusion, this increase is located between 10-100nm. This could be an effect of capillary suction because the sucked out mercury could have been hold back and, at a certain pressure, released so that the range of the pore size seems shifted.

4.2.2 Drying shrinkage parameters

During evaporative drying, the mortars have developed differently concerning the applied relative humidity values. In figure 33, the mass loss, expressed as a drying rate and plotted against time, is presented. The mortar at 43%RH evaporates slightly faster in the beginning than the one stored at 75%RH. This difference can be explained by thermodynamics considerations with a larger "drive" towards equilibrium for drying at 43% RH than at 75% RH. The difference in the system at 43%RH is larger at the beginning (the mortar specimens being fully saturated, while the desiccator being at 43%RH) than the one at 75%RH, therefore the initial evaporation is higher at 43%RH. After the first three weeks, the drying rate flattens. Overall a negative exponential-like progress is followed. As the mortar approach the RH equilibrium, the drying rate follows a constant trend at 0 mm/d (compare mortar-oSRA-75RH in fig. 33). The specimens in autogeneous conditions absorbed water at the beginning (within the first 7 to 10 days), e.g. mortar-oSRA-75RH in AC, and equilibrated at 0 mm/d afterwards.

Regarding the longitudinal shrinkage, two trends are observed, one for the specimens in AC and one for those



Figure 31: Porosity measurement results obtained by vacuum saturation and MIP for the mortars without SRA (43%RH). The measurements were performed at 42 days from casting.



Figure 32: Porosity measurement results obtained by vacuum saturation and MIP for the mortars without SRA (75%RH). The measurements were performed at 42 days from casting.

at diverse RH values. While the drying mortars shrank, those in autogenoeus conditions expanded. Due to the permanent curing in autogenoeus conditions, shrinkage is inhibited because of absent evaporation processes and even a partial compensation of self-dessication due to chemical shrinkage. Therefore, a mortar with such boundary conditions has the possibility to hydrate further without contrary side effects, hence the AC specimens slightly expanded up to 0.0003 cm/m at 112 days.

The mortars at different cast dates show the same drying behaviour by means of almost overlapping curves. In drying conditions, shrinkage was obviously expected, reflected in its monotonic decrease (and by negative values) in Figure 34. The mortar at 75%RH shrinks less than the one at 43%RH due to the boundary conditions themselves, which drive the drying process, thus the level of capillary pressure rising inside the drying pore space. If a larger amount of water is present in the surrounding atmosphere, because of higher RH, the cement-based materials will relase less water because a RH equilibrium tends to be reached sooner, with less depletion of water from the pore space and the formation of liquid water-air interfaces with larger curvature radiuses (see Eq. 2.43). Therefore, at 75%RH more water is kept in the specimen, which hinders the mortar to shrink further. In contrast, at 43%RH less water is accessable which supports greater shrinkage. The only exception to such difference between the specimens dried at two distinct RH values is visible in Fig. 33 at 112 days for the oSRA 43RH specimens. At that time a sudden steeper shrinkage decrease and a much larger error bar size, compared to those of all the other points, are visible, due to one outliner result out of the three specimens. Such large error bar differs so strongly from all the previous data that can be reasonably enough considered as a spurious outlier result.

As in Figure 35 presented, a negative exponential-like trend is recognisable for both mortar types whereby the specimens at 43%RH tend to more easily evaporate than the ones at 75%RH due to thermodynamics. At the end of the considered interval at day 112, the mortars at 75%RH reached 77%. If measured on for a further period, it is expected within two or three weeks a flattening of the internal RH curve and a constant course as indication for an achieved RH equilibrium. On the contrary, the mortars at 43%RH clearly requires a longer





Figure 33: Drying rate for the mortar specimens cast without SRA and dried either at 43%RH or 75%RH (AC - specimens in autogeneous condition)

Figure 34: Shrinkage of the mortar specimens cast without SRA and dried either at 43%RH or 75%RH (AC - specimens in autogeneous condition)

period to achieve the equilibrium. After 70 days of drying, such mortar specimens have obtained an internal RH level of 71% which is still unsufficiently close to the external RH. The latter result is consistent with the observation of similar drying rate curves for the two types of specimens.

4.2.3 Results of resonant ultrasound spectroscopies

The mortars have also been characterised by SIMO(N)RUS to detect internal changes during the drying process while progressing towards the RH equilibrium. Eiras et al. [EPB+15] have determined two main sources of influence on the linear and nonlinear dynamic elastic properties of mortars by using similar assurements as used here. The first source is the w/c ratio, the second the water saturation degree. As conclusions, they have summarised that saturation degree reduction and internal changes caused by drying affect linear and nonlinear parameters, in the specific case of linear elastic ones, the dynamic linear Young's modulus (bending modulus). They have observed that such modulus decreased with progressing drying during their experiments. They explained such decrease in terms of changes in capillary porosity content, of a decreasing hydrostatic stiffening effect and microcracking induced by drying shrinkage. In this experimental campaign, similar trends have been observed (see Fig. 36). All specimens start with a dynamic linear Young's modulus between 32 and 35 GPa on average, which is congruent with the results of Eiras et al. [EPB+15] for mortar specimens with similar w/c, even though for a slightly higher sand content (in terms of mass ratio between sand and cement, 3:1 in their case, 2.2:1 in the case of this Master Thesis project). The trend of the decrease for the different types of specimens can be sub-divided by the distinct boundary conditions. For both the specimens at 43%RH and at 75%RH, the decrease linear Young's modulus with progressing drying time seems to have occurred with similar constant speed (1st order derivative almost constant and equal for both RH levels). However, the specimens at 43%RH exhibited a sudden fall from 32 GPa to 30.5 GPa after 49 days, to rise back by 1 GPa at day 56 and continuing the originally started linear-like decreasing trend. This drop



Figure 35: Internal relative humidity development of mortar without SRA at 43%RH and 75%RH

can be explained by the sudden change in conditions from submersion in water (almost "full" saturated to the desiccator at 43%RH. The increase in Young's modulus between 49 and 56 days can have been caused by insufficient water uptake by the salt solution, so that the specimens released more water than the salt could uptake in equivalent time, resulting in a sudden increase in hydrostatic stiffening localised in time.

The specimens in autogeneous condition followed sligtly different and more contradictory trends. The specimen of the first cast (visualised by red symbols in Fig. 33) shows a similar but alleviated drop at 49 days with a further increasing course. This can result from the change in conditions as well, even when wrapping in wet cloth and storing the specimens in plastic bags kept at 90%RH is more similar to submersion. Though, the increasing trend can be caused by the further hydration resulting in increasing stiffening. In the other specimens at autogenoeus conditions, the Young's modulus grew as well except for a slight decrease at 84 days.

Eiras et al. [EPB⁺15] concluded in their 2015 article that the linear elastic moduli of the investigated mortar should be more sensitive to changes in the saturation degree itself than the nonlinear ones. The dynamic Young's modulus changes could then be used as a proxy of expresses water content changes. In contrast, changes of nonlinear moduli and even linear wave amplitude attenuation parameters, e.g., the resonance curve Q should be more sensitive to the microcracking produced by the water content changes and the respectively induced shrinkage. Therefore, SIMONRUS measurements have been performed in this project, such that further validation of that conclusion could be obtained or not.

In figures 37, 38 and 39, the resonance ultrasound spectra of the specimens drying at 75% RH are plotted at each measuring stage during the process of achieving RH equilibrium. When the resonance frequency peak shift with increase excitation amplitude is considered at first, a trend is recognisable, namely the shift increases in absolute value until day 63, after it decreases until an age of 98 days. A new increase is observable from 98



Figure 36: Dynamic Young's modulus of mortar specimens without SRA, drying at at 43%RH and 75%RH

days to 112 days, very clearly at least for one specimen (specimen 1). If the previous graphs are considered within the context of the drying shrinkage data about the same specimens, an explanation for a growth of the peak shift absolute value during the first interval (up to 63 days) can be proposed. Considering the drying rate evolution (see Fig. 33), the specimens lost water by evaporative drying the fastest during the first three weeks, which means that the internal stresses and the capillary pressure increases significantly and faster during this period than afterwards. The decrease in peak shift can be thought of occurring because an unbalancing between the crack creation and closure, both by the capillary pressure, which is continuously increasing due to the decrease in internal RH. The first specimen shows as an exception at 112 days: it exhibited again an increase. To confirm the existence of an actual increase, the specimen should have been measured upon after 119 days. Moreover, when looking at the vibration amplitude, an increasing damping is observable until day 63, followed by an amplitude growth until the end of the considered time range. Such trends are observable very clearly for all the three specimens. They mirror very accurately the trends of the peak shift. Indeed, higher/lower attenuation, which leads to lower/higher vibration amplitudes, is typically associated with an increase/decrease in crack volume or of other crack features, themselves mirrored in the increase/decrease in nonlinear elastic behaviour. The "synchronisation" between the vibration amplitude and the absolute value of the resonance frequency shift is valid even for the first specimen at 112d. It has to be reminded that the amplitude damping is strongly positively correlated with the moisture content : water filled pores damp the propagating wave due to their viscosity. However, if the amplitude would be only or prevantly coupled with the water content and not with the shrinkage and consequent cracking opening and closing, it should have continued to increase, while the amplitude clearly increased again after 63 days, for all the specimens, again with the exception of specimen 1 between 98 and 112 days. This switch in damping trend at 63 days clearly points to a coupling with the shrinkage effects. A similar coupling has been reported by Eiras et al. in their 2015 work $[EPB^+15]$.

At 43%RH, the specimens reveal a different behaviour during drying (compare Fi. 40, 41 and 42). At first sight, the peak shift varies in rather small amounts and without a generalised trend. It seems that every specimen underwent different resonance frequency shifts with increasing excitation amplitude. Widening of the shift is noticeable at 63 days, like for the specimens at 75%RH, followed by a slight decrease which varies until 112 days, where the smallest peak shift occurs. As outliner, the specimen 1 is noticeable by behaving, at 84 days, contrary in comparison to the other two specimens by undergoing a decrease in the amplitude and frequency ranges but with increased frequency shift. This phenomenon can be explained by an insufficient coupling of the specimen to the source transducer or sudden changes in the specimen due to, e.g., concentrated microcracking. Further clarification can be given by the following analysis of the nonlinear elasticity parameter a, in the next paragraph. When the amplitude is considered, slight changes are recognisable even though with no schematic trend, besides the increase in amplitude after 42 days.

Further understanding of the development of the nonlinear elastic behaviour in this type of mortar is provided the analysis of the scaling of the relative change in resonance frequency with the vibration velocity amplitude, using the same type of power law fitting procedure as used for the corresponding Vosges sandstone datasets (Sect. 4.1.3, Figs. 23 to 27). When the linear scale plot of the raw data is considered (see Fig. 43), the large variation of each value among the three distinct specimens for almost every excitation amplitude and at diverse measurement time points is outstanding when compared with the corresponding data for the Vosges sandstone specimens. This large variation could have been caused by the intrinsic microstructural inhomogeneity degree of any mortar specimen, much larger than for the sandstones. Therefore, the corresponding plot in double logarithmic scale, without the error bars, shall be in focus for the actual interpretation of the temporal development of the nonlinear elastic properties, because of easier readability. In figure 44, the development already described before for each single specimen, based on the qualitative analysis of Figs. 37 to 39, becomes evident. As it is visible in such graph, there is a clear trend : the data at each age are rather well aligned, which indicates the tendency to follow a power law-like curve; such curves, with progressing drying, tended to move to higher relative resonant frequency shift values. However, two drops in relative resonance frequency shift from one drying time to the next one are noticeable: after 63 days and after 84 days. An increase of nonlinear behaviour is represented by an upmoving of the curves, which confirms the same qualitative observation obtained from the spectra (compare with Fig. 37, 38 and 39, i.e.) that after 63 days the greatest relative resonance frequency shift was reached, thus the highest degree of nonlinear elastic behaviour. Furthermore, the slope of the curves (in the log-log plot of Fig. 46) fluctuated a lot with increasing drying time. This difference in average b value suggests a difference in nonlinear elastic behavior type. Both types of specimens exhibited predominantly a mesoscopic nonlinear elastic behaviour. On the contrary, this mortar showed a complete mesoscopic nonlinearity (average b in time of 0.63, smaller than the theoretical value of 1. This result is expectable because of the distinct microstructures of the two types of materials: the sandstone, as a consolidated granular material, has a larger volume fraction of phases (quartz and feldspar grains) which exhibit predominantly a classical nonlinear elastic behavior than the mortar (quartz grains). To assess this difference in nonlinear elastic behavior and in its temporal evolution during drying further, the fitting parameter parameter *a* and *b* have been estimated for the curves in figure 43.

Figure 37: SIMONRUS spectra of the mortar specimens cast without SRA and drying at 75%RH; age range: 42d-63d; vibration velocity amplitude [0; 6] mm/s; frequency [6800; 7500] Hz. The actual average internal RH achieved at each "drying age", for specimens of the same type and from the same batch but used only for internal RH measurements, is reported along with the "drying age". In each plot, the vertical line on the right shows the position of the resonance frequency in correspondence of the "linear" excitation amplitudes, while the vertical line on the left shows the corresponding position when the largest excitation amplitude was applied.







Figure 39: SIMONRUS spectra of the mortar specimens cast without SRA and drying at 75%RH; an age of 112d; vibration velocity amplitude [0; 6] mm/s; frequency [6800; 7500] Hz

In figure 46, b at different drying ages is presented. As the drying progressed, the b values fluctuated within the rang 0.55 and 0.65 except at 98 days, when an increase of the average of b up to 0.9 was observed, even though the error bar also increased. Such average value relates to the mesoscopic theory better. Thus, the temporal average of b, namely 0.63, can be representatively used for the actual power law fitting. When the nonlinearity strength a for both b=free and b=0.63 is considered, a peak at 63 days is unequivocally visible, indicating a local maximum in nonlinear behaviour at this drying age, in agreement with the drying rate evolution, which approached very low values after 63 days. The values and the temporal variation of the coefficient of determination, R^2 , of the power law fits does not change significantly between the fitting with two degrees of freedom (a and b) and with only one (a). Compare Figs. 45 and 47. After 63 days, a decrease is noticeable (see Fig. 44) whereby a minimum of nonlinear behaviour is observed at 98 days followed by a slight grow. Thus, it can be hypothesised that microstructural changes due, e.g., to cracking caused by drying shrinkage may have reached within the first two month a local maximum reflected into a local maximum of nonlinearity strength (a parameter). After those first two month, the specimens show a continuation in increase of capillary pressure (decrease in RH) accompanied by a decrease in nonlinearity which, as mentioned before, could be explained in terms of an overbalance of micro-crack closure in respect to micro-crack opening and new micro-crack formation, the closure being enacted by the rising capillary stress itself and, eventually, also by additional cement hydration (even though less significantly, at such late ages). At 112 days, a slight increase is recognisable, even though to be confirmed additional measurements would have been needed for further weeks, to assess the existence of an actual the trend. Therefore, such increase is here neglected. Concerning the power law fitting analysis, the plot in figure 48 presents the fitting curves of all the raw data. As concluded above, the mortars showed at 63 days the highest nonlinearity strength. Since that point a decreasing trend is observable with constant or slightly increasing amplitude. In general, the model fits the raw data quiet well except at 84 days. When the results of each distinct specimen are examined, the variation

between the specimens is rather large.



Figure 40: SIMONRUS spectra of the mortar specimens cast without SRA and drying at 43%RH; age range: 42d-56d; vibration velocity amplitude [0; 6.5] mm/s; frequency [6400; 7300] Hz

Figure 41: SIMONRUS spectra of the mortar specimens cast without SRA and drying at 43%RH; age range: 63d-84d; vibration velocity amplitude [0; 6.5] mm/s; frequency [6400; 7300] Hz



Figure 42: SSIMONRUS spectra of the mortar specimens cast without SRA and drying at 43%RH; age range: 98d-112d; vibration velocity amplitude [0; 6.5] mm/s; frequency [6400; 7300] Hz

To consider the nonlinear elastic behaviour of the mortar specimens drying at 43 %RH, the raw data (average +/- 1 standard deviation values) are shown in linear scale in figure 49. An increase in relative frequency shift, by means of rising nonlinearity, is noticeable with progressing drying age except for two drops, the first of which occurring between 42 and 49 days. At 42 days, those specimens had almost the highest relative frequency shift (in absiolute value), it dropped to a local minimum at 49 days and increased again until 84 days by achieving the highest frequency shift. Afterwards a decreasing trend is observable (see Fig. 50). By focusing on the error bar size, there seems to have been a positive correlation between them and the relative frequency shift, indicating the much higher sensitivity of the measurement to the microstructural inhomogeneity of the three specimens at peaks of nonlinearity.

By analysing the data with power law fitting, the parameter a and b provide further information. First of all, the parameter b is located within the ranges between 0.57 and 0.9. This difference suggests higher agreement with such theoretically expected value, even though at 56 days the variation of b is significant (see Fig. 51). If b is free, the parameter a, i.e. the nonlinearity strength, showed an increase at 84 days confirmed by figure 49 and 51. Overall, the drying started characterised by a high nonlinear response (at 42 days), a drop at 49 days and again an increases until 84 days followed by a decrease until the end of the measurement campaign. Mostly, the power law fitting represents the data well (see the R^2 values), besides at 49 days, where the fitting is rather poor. When the temporal average of average b values is determined and applied for the one degree of freedom fitting, the parameter a partially improves, concerning its variation and representativeness (see Fig. 53 at 42d, 70d and 84d). In general a fit was not found for the mortar specimens at different drying ages, likely due to the higher degree microstructural heterogeneity.

In Figure 54, the power law fitting is summarized as fitting curves. The less accurate fitting curves at 56 days and 84 days were probably strongly influenced by the high variation of a value between the three specimens (see Fig. 53) at 84d) and the insufficient description by parameter a expressed in R^2 (see Fig. 53 at 56d).



0.9 0.8 0.7

0.012 -

0.010 -0.008 - l ∆f_{i,0},1

0.004

0.002 -0.000.0 -0.002 -

1.0

0.3

0.1 0.0 20

erage value points reported in Fig. 43 with added Figure 48: Double-logarithmic scale plot of the avpower law fitting curves

1 standard deviation of the \boldsymbol{a} best fitting parameter mortar specimens cast without SRA and drying at obtained by the power law fitting $y = a * x^b$, R^2 is the coefficient of determination, b is fixed at 0,63.

75%RH.

4.1 1.2 - 0.6 0.4-



0.3 0.2

0.1 000 20

0.9 0.8 0.7

1.0

0.015 -

0.010

ا ∆f_{i,0},¹i,0,1

-0.005 -

0.000



parameter b

4.1 1.2 0.6 -

0.4

Figure 54: Resonance frequency shift of mortar

without SRA in logarithmic scale at 43%RH; inclu-

sive added fit

43%RH.

The trend of increasing nonlinearity strength from 49 to 84 days suggests growing imicrostructural changes by the process of drying. When the shrinkage and the internal RH changes are considered, the drying age of 84 days is a turning point, where these started to shrink less compared at previous times. After the peak at 84 days, the capillary forces reach sufficient larger values such that the amount of crack closing overcomes the opening of pre-existing ones or nucleation of new ones. The significant nonlinear behaviour at 42 days is an interesting phenomenon which suggests water having an influence on the nonlinear elastic behaviour of cement-based materials. In this case, a fully saturated mortar would show high nonlinearity strength reasoned in the damping effect of pore water moisture and hydrostatics effects on cement matrix. But to confirm this hypothesis, further measurements and research have to be done. Therefore, a founded interpretation of this phenomenon is not possible,

As a brief summary, it can be concluded the influence of water on mortar is rather small on its nonlinear behaviour, except when complete saturation is obtained. A high nonlinear elastic behaviour occurs by hydrostatic effects and damping effects. Whereas, the process of drying damages internally by capillary forces and disjoining pressure leading to microcracks. Hence, the capillary forces increase constantly, so that produced microcracks are closed by capillary forces, when they have reached a certain strength to close microcracks, and by hydration products.

4.3 Examination of mortars with SRA

A further cement-based system has been designed and adopted to try to partially uncouple the influence of drying, here in the sense of pure loss of free water from the pore space, from the influence of the shrinkage caused by the drying. This tentative uncoupling has been performed by using similar mortars as those of Section 4.2 but cast with the addition of a shrinkage reducing admixture (SRA, see Section 3.3 for

Furthermore,

details).



Figure 55: Fresh mortar properties of the specimens cats with and without SRA for a comparison.

the effect of SRA could be examined by using the same mortar mixture, but adding (except for the additive). As for the specimens without SRA, two batches of this mortar were cast on two distinct days and kept drying at the two RH values, 43%RH and 75%RH.
4.3.1 Quasi-static poromechanical parameters in fresh and hardened mortar

The fresh mortar properties of the specimens with SRA are similar to the ones without admixture. In Figure 55, the density, the porosity and the results of the slump test are shown. The fresh mortar density differed unsignificantly and can be considered as the same. Whereas, the variation in porosity is slightly higher and the mortar with SRA showed on average more air inclusions than the one without. During the mixing and testing of the mortar with SRA, it has been observed that the fresh material "foamed" and tended slightly to sedimentate, which can explain the larger porosity values. Moreover, the results for the slump are very similar as well, so that it can be summarized that the fresh mortar properties of both mortars (with and without SRA) were rather similar. After 42 days and 112 days, the density, compressive strength and the static elastic modulus were measured for all the specimens. Both mortars show enhanced densities at 42d compared with the fresh values, caused by the water saturation (the curing till that age was done by submersion in water) of the specimens and by the related higher weight. After 112 days, the specimens lost water due to the drying so that the density decreased as well.



Figure 56: Hardened properties of mortars cast with and without SRA, for comparison.

The development of compressive strength, Fig. 56, was in contrast to the mortar without SRA, chracterised by smaller variation, when comparing the results at 42 days with those at 112 days. What is clearly recognisable in Fig. 56, at both ages, lower compressive strength values for the mortar with SRA. It has been not yet completely understood, how SRA influence the compressive strength after a certain period. According to the manufacturers, SRA should have no effect on the cement hydration and on the compressive strength development. However, as the results here and in previous works show [RJ05], [BGH01], [RGC06], a decrease in compressive strength is often observed. Furthermore, the static Young's modulus, Fig. 56, varied little with drying and also differed little (slightly larger value) from the values of the spec-



Figure 57: Pore size distribution of the mortar specimens cast with SRA and to be dried at 43%RH, tested by MIP at 42nd day

Figure 58: Pore size distribution of the mortar specimens cast with SRA and to be dried at 75%RH, tested by MIP at 42nd day

imens cast without SRA. This little difference could have been caused by any SRA effect or it may also be just a random effect, due to the lack of statistical robustness of these measurements because using just one specimen was used to measure this parameter. More information about the evolution with drying of the linear elastic properties are provided in Section 4.3.3 by the analysis of what happened to the linear. When the porosity values obtained by both methods

(vacuum water saturation) and both mortar types are compared, the results for the mortar with SRA show a contrary dependence upon the measurement method compared with what obtained for of the other mortar (see Fig. 59), i.e., for the SRA specimens the porosity provided by water saturation is lower than that provided by MIP while the viceversa is true for the specimens cast without SRA. MIP seems to have provided more reliable results than water saturation because, e.g., the value of 5.9% for the specimens to be dried at 75%RH and cast with SRA is too low in comparison and for a mortar with w/c ratio of 0.5. The reason for these results by water saturation lies in the effect of SRA, where the chemical admixture contributing to the pore solution inhibits the water capillary suction, so that less water can enter the specimen, thus bias-



mortar oSRA 43RH mortar oSRA 75RH mortar SRA 43RH mortar SRA 75RH

Figure 59: Porosity results for the mortar specimens cast with and without SRA, measured by vacuum saturation and MIP.

ing the porosity measurement by vacuum saturation. In contrast, mercury has different chemical properties, therefore the SRA cannot interfere with the intruding liquid, thus more realistic porosity values can be achieved. In regard to the pore size distribution, Figure 59 implies a higher amount of smaller pores of the specimen with SRA to be dried at 75%RH, because of the difference in vacuum saturation results between both specimens with SRA and a lower pore volume than the specimen with SRA to be dried at 43%RH. This is confirmed by the MIP results shown in Figures 57 and 58. As the plots point out, the cumulative (introdued) pore volume of the mortar to be dried at 43%RH has an significant increase at 60 nm while the mortar at 75%RH at 20 nm, considering the first intrusion curve for both specimen groups. In general, it is recognisable that the pores of the specimen at 43%RH are distributed between 30μ m and 3 nm and the mortar contains a total specific pore volume of 70 mm³/g. The other specimens to be dried at 75%RH, exhibits the same pore radius range but a total specific pore volume of 60 mm³/g.

4.3.2 Consideration of drying shrinkage parameters

A SRA is typically used to reduce shrinkage. It does so mainly by lowering the surface tension of the pore solution, thus lowering the magnitude of the capillar pressure rising up due to evaporative drying. As described in Section 2.3.5, one of the original targets in this experimental campaign consisted of trying to reduce shrinkage without altering significantly the drying itself, in order to uncouple the effects of a decreasing saturation degree from the effects of the accompanying capillary pressure rise within the pore space. When the drying rate for the specimen with SRA is considered, the curves show an equivalent trend as the one without SRA, but in a softened way (see Fig. 33 and60), whereby the curve of the mortar drying at 75%RH developed more linearly, indicating a slower falling rate. In general, the drying rate for both types of SRA specimens shows smaller values than the specimens without SRA. On the contrary, the results reported here support the conclusions of Bentz et al. [BGH01], who observed, for cement pastes cast without and with a SRA, that the SRA led to drying time scales and a more uniform distribution of the water in the material. The SRA reduced shrinkage, especially at the beginning of the drying process, as it is observable in Figure 61.





Figure 60: Drying rate for the mortar specimens cast with SRA and drying at 43%RH or at 75%RH (AC - autogeneous conditions)

Figure 61: Shrinkage of the mortar specimens cast with SRA and drying at 43%RH and 75%RH (AC - autogeneous conditions)

Important to be remarked at this point are problems encountered during the experimental campaign with the drying of the set of specimens to be dried at 43% RH. The RH in the dessicator where such specimens were stored fluctuated significantly in the dessicator and for the majority of the time could not achieve values

lower than 70 - 80%. Thus, the drying for the specimens labelled as SRA 43RH is expected to have occurred rather similarly to the drying for the specimens dried at 75% RH, which were not affected by such a problem. Similarly, as for the mortar without SRA, the specimens in autogeneous conditions expanded with a maximum relative length change of 0.0002 cm/m, as for the specimens in auotgeneous conditions without SRA. Even the trend is almost the same as for the specimens without SRA. A small difference in final shrinkage is observable between the two SRA AC mortar specimens, with the mortar (SRA-75RH in AC) having shrunk less than the other in autogeneous conditions. In contrast to the mortars without SRA, where the shrinkage developed according to a negative exponential-like behaviour, a linear trend is noticeable for the SRA specimens (compare Fig. 34 with Fig. 34). Such linear-like progress reveals that the SRA led to a constant-like shrinkage rate likely related with water in the specimens. Moreover, the mortar shrank less than 0.0004 cm/m, which was the value both types of dried oSRA specimens overcame.

The development of the internal relative humidity followed the same "scheme" related with a spatial-temporal homogeneous loss of water. Hence, a linear-like progress of decrease in relative humidity is visible in figure 62. The high degree of overlapping of the two curves in the same figure is due to the similarity in external RH achieved for both sets of specimens, instead of achieving a lower value (about 43%) for one of them.



Figure 62: Development of the internal relative humidity in the mortar specimens cast with SRA at 43%RH and 75%RH

4.3.3 Results of resonant ultrasound spectroscopies

Equivalent to the mortar without SRA, it is expected that the dynamic linear elastic behaviour, during the drying should develop similarly to what happened for the mortar cast without SRA, i.e., decrease in dynamic Young's modulus and an increase, at certain ages, in nonlinear strengths with ongoing drying are expected.

However, since it is also expected that the microcracks development should differ, based on the influence of SRA, different ranges of decreases and increases for the two types of parameters should be foreseen as well. At first, the linear elastic behaviour is considered. In Figure 63, it is noticeable that the variation for all specimens was rather small, for example 3 of 4 curves starting at about 32.7 GPa and the curves, in general, having a much higher degree of overlapping (considering the error bars) than in the case of the specimens cast without SRA. Moreover, the specimens in autogeneous condition followed an upgoing trend as in mortar without SRA, caused by hydrostatic stiffening and the achievement of higher hydration degrees than the corresponding drying specimens. In contrast, the drying specimens exhibited a decrease in linear Young's modulus as already observed for the oSRA specimens and as shown by Eiras et al. [EPB⁺15] as well. However, the mortar drying at 75%RH showed an interesting slight increase in linear Young's modulus during the first three weeks (42d-63d). This phenomenon could be explained by another spuious effect related with the conditions inside the desiccator : the solution of potassium chloride, used to achieve an environmental RH of 75%RH, could not immediately lead to the set value because of different rates of water loss by the specimen and uptake by the solution itself.

As such, these specimens were kept inside the desiccator at an external RH slightly higher than 75%, leading to boundary conditions more similar to the autogeneous conditions than to the drying ones. Moreover, the partial of water retention-like effect by SRA could prolonged hydrostatic stiffening, contribution to a larger scatter in the results, thus making the trend seems to rise although it could have been actually constant as well.



Figure 63: Development of dynamic Young's modulus in mortar with SRA and drying at either 43%RH or 75%RH.

When the nonlinear behaviour is examined, the spectra of the specimens drying at 75%RH already illustrate the type of pattern for its temporal evolution with the decrease in internal RH (see Figs. 64, 65 and 66). First, the resonance frequency shift is considered to describe the pattern. With progressing drying time, an increase in resonance frequency shift is noticeable until 70 days. This is clearly observable for each of the three specimens. Afterwards, it diminished again, to exhibit again an increase between 98 days and 112 days. This common pattern indicates a rise in nonlinearity until day 70 and a possible starting increasing trend at day 112 day. To analyse the actual existence of this starting trend, it should be observed in following measurements as well. The data for the first specimen at 84 days are an outlier compared with this common pattern. At such age that specimen exhibited a very large resonance frequency shift, a very small vibration amplitude and an overall huge decrease in the resonance frequency at the smallest vibration amplitude values, all of which differ from any other result for that specimen at any drying age and for the other specimens as well. These outlier data are most likely explainable by measurement implementation problems, e.g., a poor coupling between the specimen and the source transducer.

Second, the vibration velocity amplitude in correspondence of the largest excitation amplitude is considered as an indicator for the temporal evolution of the wave amplitude damping. A constant decrease of such maximum amplitude is observable with progressing drying age until 70 days, after which a partial increase is observable without a complete recovery of the starting values at 42 days. Such decrease in maximum vibration amplitude until about 70 days means an increase in amplitude attenuation till that age. Such a trend couples well with the qualitatively observed increase in nonlinearity till the same age. A similar coupling was already observed for the oSRA 75RH specimens. Again a stronger coupling between attenuation and non-linearity than between attenuation and saturation degree is observed here, as observed for the oSRA 75RH specimens as well and as observed by Eiras et al. [EPB⁺15]. Third, the resonance frequency values always fall in the same range, between 7100 and 7200 Hz, except at 70 days. There is a shift of the range to a center value about 7000 Hz noticeable which supports the interpretation of a certain increase in nonlinearity after 70 days. This point will be analysed in the following paragraph.

The trend for the mortar specimens dried at the nominal 43%RH is in general less unambiguous than the one at 75%RH. More often a specimen differs in frequency shift, amplitude or frequency range from the other two (see Figs. 67, 68 and 69). First of all, the resonance frequency shift is considered. Generalised, it can be observed, that with progressing drying age, the absolute value of the resonance frequency shift increased as it happened for the mortar specimens drying at 75%RH but until 84 days, not 70 days. Since 98 days, a decrease is observable. The exception is provided by specimen 3, whose resonance frequency shift did not start to decrease after that age, likely caused by some specific and higher degree of microstructural heterogeneity, compared with the two other specimens and those drying at 75%RH. When the vibration amplitude is examined, a damping is noticeable until 63 days. For the mortar specimens drying at 75%RH, the amplitude decrease continued until 70 days. To analyse all of these trends quantitatively, the power law fitting analysis was also performed for the SRA specimens. In figure 70, the average value +/- 1 standard deviation of the absolute value of the relative change 8shift) in resonance frequency as a function of the corresponding vibration velocity amplitude is shown in linear scale, for each age. In comparison with the corresponding data for the specimens cast without SRA, the error bars in this figure are in general smaller, their largest values having been achieved at 98 days. It needs to be remarked here that the results at 42 days differ from the other ones because of the measurements were performed without implementing the Haupert's protocol [HRR⁺11]. Therefore, this measurement point has been excluded from the analysis (see Figs. 71, 72, ..., 75). Thus, the results in Figure 71, reporting only the average values shown in Fig. 70, but in double logarithmic scales, show an increase in nonlinearity strength until 70 days, where the highest relative frequency shift occurred followed by a drop at 84 and 98 days. A starting increasing trend at 112 days could be hypothesized but would require, as in the case of the specimens cast without SRA, further measurements. Hence, a peak in nonlinear behaviour is suggested to have occurred at 70 days, a result already shown, even though even more qualitatively, by Figs. 64 to 66.



Figure 65: SIMONRUS spectra of the mortar specimens cast with SRA and drying at 75%RH; age range: 70d-98d; vibration velocity amplitude [0;6,5] mm/s; frequency [6600;7300] Hz

Figure 64: SIMONRUS spectra of the mortar specimens cast with SRA and drying at 75%RH; age range: 42d-63d; vibration velocity amplitude [0; 6,5] mm/s; frequency [6600; 7300] Hz



Figure 66: SIMONRUS spectra of the mortar specimens cast with SRA and drying at 75%RH; age: 112d; vibration velocity amplitude [0; 6,5] mm/s; frequency [6600; 7300] Hz

This conclusion can be better supported by the analysis of power law fitting analysis. In Figure 72, the nonlinearity strength, embodied by the fitting parameter a, inclusive the coefficient of determination is presented in the case of the fitting including b as fitting parameter (two-degree of freedom fitting). At early ages, a high variation in the coefficient of determination, i.e., in the goodness-of-fit, and, particularly, in the parameter a at 49 days is recognisable. Hence, a description of the experimental data by the theoretical power law model function is, especially in the beginning of the drying process, less reliable, likely because of the slower drying (smaller drying rates, see Fig. 60) compared with the specimens cast without SRA, resulting in higher variation in nonlinearity strength and power law exponent b (see Fig. 72 and 73). Notice that this result is not in contradiction with what mentioned above about smaller error bars for the relative changes in resonance frequency and in vibration amplitude: the error bars are smaller for the SRA specimens. However the dependency of the first variable from the second one agrees less with the power law model, at the beginning of the drying. Despite such lower level of reliability of the power law fitting results, a peak in a is rather clearly visible at 70 days, as also observable from the resonance curves plots themselves (Figs. 64 to 66). As in figure 70 and 71 already noticeable, it seems that a further increase in nonlinearity started at 112 days. When b is considered (see Fig. 73), its values varied between 0.45 and 0.9, with an average value in time of at 0.73, about which most of the values are located. The more reliable description of b were achieved at 70 days, 84 days and 112 days. By fixing b to 0.73, the variation of the nonlinearity strength a at 49 days could be limited to a significant smaller range. Concerning the coefficient of determination, a is better estimated at 70 and 98 days by the fitting with free b than with fixed b. Therefore, it is complicated to chose an optimal value for b. Nevertheless, the chosen fit in figure 75 with b = 0.73 reflects the raw data well.

The specimens dried at the nominal 43%RH should have followed similar trends as those dried at 75%RH, because of the problems encountered in achieving in the dessicator where they were stored for drying the target RH, rather achieving a similar value of about 75% as for the other specimens. A peak in nonlinearity strength a is observable for the SRA 43%RH specimens as well but at 84 days, not at 70 days. As by the mortar drying at 75%RH, the resonance frequency relative change versus vibration amplitude curves dropped after the peak significantly. However, in contrast to the 75%RH specimens, they continued decreasing (see Fig. 76). When the nonlinearity strength is included in consideration (compare Fig. 78), the same trend is observable, whereby a decrease of a is better noticeable at a drying age of 70 days.





Figure 68: spectra of the mortar specimens cast with SKA and drying at 43%RH; age range: 63d-84d; vibration velocity amplitude [0; 6,5] mm/s; frequency [6600; 7300] Hz



Figure 69: SIMONRUS spectra of the mortar specimens cast with SRA and drying at 43%RH; age range: 98 and 112d; vibration velocity amplitude [0; 6,5] mm/s; frequency [6600; 7300] Hz

This phenomenon is explainable by unexpected effects of SRA to re-distribute homogeneously the water in the specimen reducing the stresses and strains caused by internal RH gradients or sudden microcracks closure by late hydration. Moreover, the scatter of the *a* values over the three distinct specimens increased with increasing average values of the same a fact clearly visible from both fittings (see Figs. 78 and 80). By strengthening the nonlinear elastic behaviour of the specimens likely due to the formation of microcracks, each specimen exhibited quantitatively a different developments in nonlinearity, thus the standard deviation increases. In consideration of the coefficient of determination of the fitting, a similar progress as at 75 %RH is noticeable, where at young drying ages, R^2 was very large and, after 2 weeks of drying, it decrease to values entitling the fitting of more reliability. When the parameter b is considered, it achieved for the SRA 43%RH specimen values within the range 0.65 and 0.8, comparably smaller than the range at 75%RH (compare Fig. 73 with 79). Furthermore, a decreasing trend for b is recognisable with progressing drying age (Fig. 79). If the temporal average is calculated, a value of 0.7 is found, which was used for the fitting with a fixed parameter b. To compare the development of parameter a between the two types of fitting of the SRA 43Rh data, it differs slightly, whereby a better description is achieved by a fitting with a fixed slope at 0.7 (compare 42 days and 70 days in figures 78 and 80). This is reflected in figure 81, where the fitting curves are located closely to the raw data in double logarithmic scales. At 49 and 63 days, the fitting lines are situated slightly above the data points, caused by the large variations between the various specimens.

As summary of the nonlinear elastic behaviour evolution with drying, for specimens cast without and with SRA, it can be concluded that, at the beginning of drying, the mortars did not show a very strong nonlinearity, as Eiras et al. [EPB⁺15] already pointed out, besides the specimens without SRA at 43%RH which can be considered as an exception, likely due to a stronger initial drying (these are the specimens for which the drying rate and the linear shrinkage achieved highest absolute values at 49 days).



 R^2 is

0.3 0.2

0.1 0.0 20

110

100

0.8 0.7

0.9



Figure 74: Average value (black square markers) +/-1 standard deviation of the \boldsymbol{a} best fitting parameter obtained by the power law fitting $y = a * x^b$, R^2 is the coefficient of determination, b is fixed at 0,73.

Figure 73: Development of the fitting parameter b(power law fitting function $y = a * x^b$) for the mortar specimens cast with SRA and drying at 75%RH.



Figure 76: Absolute value of the relative resonance frequency change (shift), $|(\frac{\Delta f_{i,0}}{f_{i,0}})|$, as a function of the resonance vibration amplitude, plotted in linear scale on both axes for the mortar specimen cast with SRA and drying at 43%RH



Figure 79: Development of the fitting parameter b(power law fitting function $y = a * x^b$) for the mortar specimens cast with SRA and drying at 43%RH.



Figure 77: Double-logarithmic scale plot of the average value points reported in Fig. 76.



Figure 80: Average value (black square markers) +/-1 standard deviation of the a best fitting parameter obtained by the power law fitting $y = a * x^b$, R^2 is the coefficient of determination, b is fixed at 0,7.



Figure 78: Average value (black square markers) +/-1 standard deviation of the a best fitting parameter obtained by the power law fitting $y = a * x^b$, R^2 is the coefficient of determination (mortar: with SRA, drying at 43%RH)



Figure 81: Double-logarithmic scale plot of the average value points reported in Fig. 76 with added power law fitting curves

Moreover, the mortars show a peak in nonlinear elastic behaviour (compare parameter a) between 63 and 84 days, depending on the external RH value of drying and on the specimen realisation (the SRA specimens were all dried, factually, at the same external RH, even though the two sets of them exhibited peaks in a at different ages). Furthermore, a difference in the a values between the specimens with SRA and without is exposed : By reducing drying evoked cracks due to the SRA, the nonlinearity strength a in mortar with SRA is weaker than in specimens without SRA. As in literature suggested [EPB⁺15], the parameter a is proposed as an index for the sensitivity to microcracking in early ages of cement-based materials, which is also reflected in this Master Thesis by connecting the shrinkage behaviour with the development of a. Thereby, a relation is recognisable supporting those conclusions.

4.4 Comparison of the elastic behaviour of the Vosges sandstone with that of the mortars, during evaporative drying

In the previous sections, the materials, sandstone and mortars, have been analysed concerning various parameters focusing on their (linear and nonlinear) elastic behaviour and their evaporative drying-induced reaction on shrinkage. Thereby, multiple differences have been shown which are more closely considered in this section. By starting with the comparison of the porosity, it can be easily noticed in figure 82 that the sandstone is more porous than the mortars. Moreover, the pore size distribution differs significantly, whereby the sandstone shows mainly pores in size of 10 to 25 μ m and mortar primary in smaller ranges of 10 to 100 nm. These distributions explain the differing drying behaviour : the sandstone can achieve significantly faster the equilibrium between the external and internal RH (ca. 1 week) than the mortars (more than 2 months needed). The achievement of the equilibrium is important because it means, in principle, achieving also a spatial homogeneous distribution of saturation degree, which should stop the shrinkage, thus the corresponding cracking, in correspondence of which the non-linear elastic behavior could be expected to be maximized (at least for the mortars, where the cracks are expected not to be closed in large volume fractions by the capillary stresses generated by the decreased RH).

When the drying rate is considered (see Fig. 83), it is evident that the sandstone lost less fast (free) water (2,5 mm/d) than the mortars (5,7-13,7 mm/d), even though, the drying behaviour was similar by following a negative exponential progress until approaching 0 (for the mortars specimens cast without SRA, more linear-like for those cast with SRA, which decreased the initial drying rate as well, bringing it closer to the value for the sandstone). These differences in water loss (drying) rate were also due to the pore size distribution: with a larger pore volume fraction due to much smaller pores, capillary pressure rising during drying produce, especially during the constant drying rate period, faster displacement of water towards the open boundary surface. Indeed, as already observed by Yang et al. [Ya16b], [Ya16a], the constant rate period is typically much shorter for mortars than for stones, because of larger drying rates during it, due to higher capillary pressure gradients developed during it.

As expected, the shrinkage development of both materials differed strongly : the sandstone shrank slightly, almost neglectably (see Fig. 84 compared with the mortars). The mortar showed higher values from -0.0003 to -0.0009 cm/m depending on the addition of SRA or not and on the external relative humidity driving the drying.



Figure 82: Summary of results of vacuum saturation and MIP porosity and pore size distribution assessment for the Vosges sandstone and the mortars



specimens

Figure 83: Summary of the drying rates of all the Figure 84: Summary of shrinkage development of all the specimens

The drying behaviour can be further described by the development of the internal RH (see Fig. 85). As the sandstone nearly progresses linearly in correspondence to the external RH value, the mortar with SRA behaves similarly in time, but took more time to approach equilibrium. Due to the effect of the SRA, a linear evaporation process is forced so that shrinkage is reduced by keeping the water release almost constant and distributing the water homogeneously in space, thus decreasing internal RH spatial gradients. For mortars without SRA, a negative exponential trend is observable, driven by a faster decrease towards the external, i.e., equilibrium value. By means of Figure 85, the difference in the velocity of drying processes is pointed out well.

In consideration of the elastic behaviour, the evolution of the linear Young's modulus is compared at first (see Fig. 86). To begin, the range of values is compared, whereby the Vosges sandstone exhibited values between 15 and 19 GPa and the mortars values between 30 and 34 GPa. That means that the mortars are stiffer than the sandstone having a higher resistance against elastic deformations. Furthermore, opposite trends for the two types of materials are observable, whereby the linear modulus of the sandstone increased with progressing drying while the mortars showed a decrease. These distinct trends can be understood in terms of the different role played by water in the two types of porous materials. While water plays, for the Vosges sandstone, mainly the role of a pore space filler, with minor chemical and microstuctural interaction with the clay particles, which contribute to only 5 - 10% of the total volume of a specimen, its microstructural role is much more relevant in the mortars, where it does not only fill the pore space but actively contributes to the microstructure itself, in the form of chemically absorbed water in the cement hydration products. Even though the drying investigated in this work was at still relatively high external RH values, not sufficient to lead to dramatic structural changes of the hydration products, especially to the structurally layered ones, as the C-S-Hs, such "weak" drying process could have started to perturb the molecular structure of such calcium silicate hydrates [BRAM10], [BGUL16]. The stiffening of the sandstone with the increasing lost water can



Figure 85: Summary of the development of the internal RH of all the specimens.

Figure 86: Summary of all the linear Young's modulus progress with drying of all the specimens.

thought of being mainly due to the rise in the capillary pressure due to the formation of the water-air menisci in the pore space of porous material whose solid frame/skeleton is essential not perturbed by the loss of water itself, from the molecular structure point of view. The same capillary pressure rise, even stronger, occurred for the mortars but with an additional modification of the solid skeleton itself. One could think of a sandstone solid skeleton with unvaried and unscathed elastic moduli, while the elastic moduli of the mortars solid skeleton decreased along with the decrease in saturation degree. if the capillary pressure in the sandstone just "consolidated" the porous material, closing cracks, it contributed to open new ones in the mortars, letting the solid skeleton start to decompose.

Such modification of the molecular structure of the solid skeleton in the mortars is reflected even more in the changes of the nonlinear elastic behaviour (see Fig. 87). Considering the nonlinearity strength a, the Vosges sandstone showed decreasing values with decreasing RH values. The "compaction" effect of the rising capillary pressure without the generation of new crack volume dominated. In contrast, the mortars presented more variegated trends by showing more scatter in the nonlinearity strength values for distinct specimens. Despite such higher scatter, a general pattern was clearly observed. It is noticeable that the nonlinearity of the mortars increased with progressing drying age, but just until they reach a certain point in nonlinearity (63-84 days), to decrease afterwards. Hence, it can be concluded that mortars are less sensitive to free water content than to microstructural modifications brought by the continuous rise in capillary stresses produced by the drying. In contrast, the nonlinearity strength of the Vosges sandstone is directly related to the moisture content itself, even though it has to be remarked once more that the mortars did not reach yet the external-internal RH equilibrium during the experimental campaign, contrary to what the sandstone did, so that a direct comparison between of the results between the two types of materials is not completely possible. When the power law exponent b of both materials is considered, it is noticeable that the sandstone had a temporally averaged value of 1.33, which is above the mesoscopic theory value of 1, thus pointing to a predominate mesoscopic nonlinearity still mixed a classical one, likely due to the nonlinear response of the single grains of the sandstone, while the mortars achieved average values between 0.63 and 0.73, mesoscopic theory nonlinear elasticity only.

As conclusion, it can be summarised that the Vosges sandstone reveals a quiet different drying and elastic behaviour than the mortars. This is caused by the microstructural properties, in terms of pore space features and properties of the solid skeleton itself. Moreover, mortars are more inhomogeneous systems than the sandstone, whereby higher variations in the results occur and the interpretation becomes more difficult and not as clear. Thus, the sandstone linear and nonlinear elastic behaviours depend predominantly on the water saturation degree itself, i.e. on the water content, while the mortars' on the damaging processes associated with changes in the saturation degree.





5 Conclusions and outlook

Linear and nonlinear single mode RUS measurements have been applied to a type of Vosges sandstone and two types of mortars during the process of drying. When considering the elastic behaviours of both materials, the sandstone revealed a strong (if not complete) dependence on the saturation degree itself, without significant dependence on microcracking, which likely occurrs relatively little during the drying, as already pointed out in the existing literature [VCJZ02]. However, a slightly differing development in nonlinear elastic behaviour than what reported in existing publications (compare with [VCJZ02] and [JS05]) was also observed. The examined Vosges sandstone exhibited monotonical changing in linear Young's modulus and nonlinearity strength by the decrease in water saturation degree or, rather, in moisture content. It "hardens" with decreasing moisture content. This was already reported in the literature. In mesoscopic nonlinear elastic behaviour with decreasing moisture content, mainly due to the corresponding rise in pressure, cracks close without opening new ones, thus leading to a sort-of macroscopic "consolidation" or "stiffening" of the stone and a decrease in its nonlinear elastic behavior.

On the contrary, the mortars exhibited a clear trend in the linear elastic behaviour, with a decreasing linear elastic modulus with diminishing moisture content, due to not only changes in the water content but also to microstructural changes to the solid skeleton of such porous materials, the nonlinearity strength changed even stronger to the solid skeleton microstructural changes caused by the drying and such changes were assessed to be mainly related with such microstructural changes towards the beginning of the drying process, while they got influenced by the water content changes as well later on. Surely, the water saturation degree and the drying shrinkage are tightly coupled with each other, at the point of missing a starting target of this work, i.e., obtaining a similar water saturation degree but a different drying shrinkage in the mortars, by using SRA. However, depending on the level of drying, the mortars showed the strongest nonlinear behaviour only at specific moments during the drying, when the drying gradients seemed to be the greatest and/or the corresponding internal capillary stresses caused the most of the microcracking, suggesting a high sensitivity of the nonlinear elastic response on the microstructural changes, thus confirm the advantage of nonlinear elasticity measurements over linear for the detection of micro-damage, even in the presence of "mild" driving damage processes as drying shrinkage at intermediate levels as obtained in this study, with still rather high external relative humidity values. The usage of SRA for uncoupling water saturation degree changes from shrinkage failed. However, it was possible to partially investigate its role on the evolution of the linear and nonlinear elastic behaviours of mortars. SRA seems to influence indirectly the elastic behaviour of mortars by decelerating the drying process and partially inhibiting shrinkage-induced cracks, as expectable. Therefore, mortars cast with SRA varied less in linear elastic modulus and showed smaller nonlinearity strength. By adding SRA to the mortar mixture, the specimens dried monotonically so that the influence the of water

saturation varied less and was easier to evaluate. Additionally, SRA reduced the creation of drying shrinkagerelated cracks, as expected. Nevertheless, the uncoupling of influences caused by water changes in mortar and by microcracking is not feasible and therefore at most, a qualitative consideration in comparison to the mixture without SRA would be possible. In contrast, the sandstone reacts indeed to internal water changes but rather little to related cracking (see Fig. 84). Therefore, it can be suggested that the uncoupling of influences of Vosges sandstone is more applicable than the one for mortars. Finally, the comparison of the results for the Vosges sandstone with those for the mortars is at this point still not completely meaningful because of the non-reaching of equilibrium by the mortars specimens. Therefore, further measurements in equilibrium shall be performed to compare the two materials in the same thermodynamic state and to evaluate the behaviour of mortars in non-equilibrium and in equilibrium. Furthermore, an additional desorption step should be performed to observe the (linear and nonlinear) elastic behaviours of the Vosges sandstone at a RH value lower than 14%RH to completely and unequivocally confirm the differing trend of the sandstone from the one so far published [VCJZ02] and [JS05].

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