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# Validation of *in situ* applicable measuring techniques for analysis of the water adsorption by stone

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## Abstract

As the water adsorbing behaviour (WAB) of stone is a key factor for most degradation processes, its analysis is a decisive aspect when monitoring deterioration and past conservation treatments, or when selecting a proper conservation treatment. In this study the performance of various non-destructive methods for measuring the WAB are compared, with the focus on the effect of the variable factors of the methods caused by their specific design. The methods under study are the contact-sponge method (CSM), the Karsten tube (KT) and the Mirowski pipe (MIR). Their performance is compared with the standardized capillary rise method (CR) and the results are analysed in relation to the open porosity of different lithotypes. Furthermore the effect of practical encumbrances which could limit the application of these methods was valuated. It was found that KT and CSM have complementary fields of investigation, where CSM is capable of measuring the initial water uptake of less porous materials with a high precision, while KT was found commodious for measuring longer contact times for more porous lithotypes. MIR showed too many discommodities, leading to unreliable results. To adequately compare the contact material and pressure on the surface do not indicate a significant influence on the results. The study of these factors is currently being extended by visualization of the water adsorption process via X-ray and neutron radiography in combination with physico-mathematical models describing the WAB.

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# 1. Introduction

Natural stone is an elementary material when considering our cultural heritage. It is utilized for architectural purposes such as facades and their ornaments or for sculptural purposes. In the last decades atmospheric pollution has become one of the main factors accelerating stone degradation processes [1, 2, 3]. Within the area of conservation sciences, the assessment of these degradation processes is substantial for preventive conservation purposes, as well as monitoring of the effectiveness of past restoration treatments. A key factor for most stone degradation processes is the infiltration of water in porous stone materials. Consequently, the water adsorbing behaviour (WAB) of stone is a significant factor for its conservation and determines its propensity to future deterioration [4]. Additionally, changes in the WAB can be an indication of the degree of deterioration or the effectiveness of past treatments, e.g. a water repellent treatment [5]. Hence, analysis of the WAB is a decisive aspect when monitoring deterioration of stone and past conservation treatments, or when selecting a proper conservation treatment.

The WAB can be defined as the extent to which water is adsorbed and retained in the stone structure. Physical properties related to each specific lithotype, namely the open porosity, the pore size distribution and the pore structure or their tortuosity and interconnectivity [6] determine the WAB. Even though these properties can be analysed separately in laboratory by means of, respectively, water adsorption under vacuum [7], intrusion porosity measurements such as mercury intrusion porosimetry [8, 9, 10] and X-ray or neutron µ-CT scanning [11, 12], it is their synergy which determines the actual WAB. Methods for measuring this overall WAB are based on a general principle: water is brought in contact with the stone surface and the amount of water adsorbed in function of time is recorded. Examples of the most commonly used measuring techniques for the WAB are the Capillary rise method (CR), the Karsten tube (KT), the Contact-sponge method (CSM) and the Mirowski pipe (MIR). Moreover, constant attempts are made on developing adaptations on the already existing techniques and new techniques [13, 14]. Even though all these methods are based on the same principle, the methods are developed with different specific aims (e.g. monitoring the breakthrough through hydrophobic barriers, measuring very low levels of water adsorption), leading to differences in design and practical application. Recent research on the comparison of these different techniques [15] illuminated the fact that these differences in design influence the measurements as the results of the different methods are related, but cannot be compared as easily. Furthermore, concerning the application, at present none of these methods is standardised, leading to different interpretations of the application procedure by the operators, thwarting the comparison of results.

When referring to the practical field, it is observed that the different methods are used [5]. The selection of the methods used depends mainly on the specific aims, the availability of the methods and the common practice. A decisive characteristic of the methods is their (non)-destructiveness. Destructive techniques, such as CR, require a sample taken from the bulk, which is not an option in case of monitoring (where the same exact area is repeatedly measured in time) or analysis of sculptures or other materials with high value. In contrast, KT, CSM and MIR are developed especially for non-destructive, *in situ* application. The *in situ* methods have a second advantage that multiple measurements on different positions can be done more easily (non-destructive), increasing the reliability of representative sampling in non-uniform materials/structures.

This paper presents a part of a larger study, which focusses on the comparison of non-destructive techniques for analysis of the WAB, in order to develop a methodology for selection and application of the methods and an adequate comparison of results. This paper focusses on the influence of the variable factors of the methods related to their specific design. Therefore the results of repeated measurements with the various methods on seven lithotypes are compared and the influence of the differences in practical application and design is studied.

# 2. Materials and methods

#### 2.1. Conditions and materials tested

As non-destructive methods are developed for use in situations where destructive sampling is not an option, most investigations take place *in situ*, where variable factors such as climatic conditions, moisture content of the stone, biological growth, fouling,... can influence the measurement. To exclude these variables, all methods have been scrutinized in laboratory environment (average temperature of 20-22°C and 55% RH) on stone samples in a first stage. All samples were dried in an oven at  $60 \pm 5^{\circ}$ C until the constant dry mass (CDM) was reached, according to UNI/NORMAL 10859 [16]. To maintain the CDM the samples were kept in a desiccator when cooling down to room temperature. Weight measurements were made with a balance with a precision of 0.001g. Only distilled water was used.

For the validation of the different methods seven porous lime- and sandstones with a varying open porosity were chosen. The selection was based on lithotypes that are widely used for architectural and sculptural purposes in Belgium. Table 1 gives an overview of the properties of the selected stones. The real density and open porosity have been determined by the Belgian Building Research Institute [17, 18, 19]. For each lithotype the samples (7 x 2 cm<sup>3</sup>) were cut from a bigger stone slab to obtain samples with technical properties as similar as possible.

Lithotype	Symbol	Real density (kg/m <sup>3</sup> )	Open porosity (%)
Massangis Roche Claire	MC	$2427 \pm 5$	$10.7 \pm 0.2$
Massangis Roche Jaune	MJ	$2400 \pm 120$	$10.5 \pm 0.9$
Senonville	S	$2388 \pm 7$	$10.6 \pm 0.2$
Valanges	V	$2300 \pm 100$	$14 \pm 2$
Magny Doré	М	$2290 \pm 20$	$15.6 \pm 0.8$
Tercé	Т	$2060 \pm 75$	$24 \pm 5$
Estaillades	E	$1920 \pm 20$	$29.3 \pm 0.6$

Table 1. Average values of the real density and open porosity of the selected lithotypes

#### 2.2. Methods

#### 2.2.1. Capillary Rise method (CR)

For comparison of the methods, CR measurements were performed according to UNI/NORMAL 10859, as this setup is more similar to CSM than the setup of DIN 52617. For the UNI/NORMAL 10859 a stone sample is placed on a pile of humid filter papers, allowing the stone to adsorb water by upward capillary forces (Fig.1a). After the fixed contact time the samples are withdrawn, water on the surface which has not been adsorbed is removed using a humid cloth and the samples are weighed. In order to analyse the possible influence of the filterpapers on the measurement, a number of comparative tests were made according to DIN 52617, where the stone surface is brought in direct contact with the water. The WAB for both procedures is calculated according to Eq. (1), where A equals the contact area between the sample and the humid paper or the water;  $\Delta m$  the amount of water adsorbed, which is calculated by subtraction of the initial mass  $m_i$  from the final mass  $m_f$  of the stone sample and t the time in seconds.

$$Wa \left(g/m^2, s\right) = \frac{\Delta m}{A \cdot t} = \frac{\left(m_f - m_i\right)}{A \cdot t}$$
(1)

#### 2.2.2. Karsten tube (KT)

The Karsten tube is an open glass tube with a larger cylindrical body at the end which is sealed to the surface of the stone by plastiline (Fig.1b). Once attached, water is added to the tube and the amount of water adsorbed over a certain period of time can be recorded by measuring the reduction of the water volume in the graded tube. The gradations go from 0 to 4 ml, divided in sub-gradations of 0.1 ml. The water column has a height of 9.8 cm, measured from the start of the gradations to the centre of the cylindrical body, exerting a pressure on the stone surface of 961.38 Pa. This pressure corresponds with rain drops hitting the wall with a static wind velocity of 140 km/h, perpendicular to the surface [20], in order to analyse if water can penetrate through a hydrophobic barrier in case of heavy rainfall. The WAB was calculated according to Eq. (1), where A equals the surface of the cylindrical body (0.000573 m<sup>2</sup>) and  $\Delta$ m equals the amount of water adsorbed over the contact time t. According to the RILEM II.4 recommendation [21], measurements were performed after 5 and 15 min contact time to calculate the WAB between the 5th and 15th minute ( $\Delta$ 5-15 min) according to Eq. (2).

$$Wa_{\Delta 5-15\min}(g/m^2.s) = \frac{(m_{(15\min}) - m_{(5\min}))}{A \cdot t_{10\min}}$$
(2)

#### 2.2.3. Contact-sponge method (CSM)

The Contact-sponge method was developed in 2004 by Tiano and Pardini [22]. The method consists of a sponge (type Calypso natural make-up from Spontex<sup>®</sup>), enclosed in a 1034 Rodac<sup>®</sup> contact plate (Fig.1c). The contact plate is composed of two parts, namely a base and a cover. The diameter of the sponge corresponds with the inner diameter of the base, whereas the height of the sponge exceeds the vertical borders of the base. For the measurement the cover of the contact plate is removed, water is added to the sponge and the sponge enclosed in the contact plate is weighed (m<sub>i</sub>). After weighing, the cover of the contact plate is removed and the sponge is pressed manually against the stone surface until the vertical borders of the base touch the stone surface. After the selected contact time, the contact sponge is removed and weighed inside the closed contact plate (m<sub>f</sub>). The WAB is calculated according to Eq. (1), where A equals the surface of the sponge (0.002376 m<sup>2</sup>);  $\Delta m$  the amount of water adsorbed from the sponge (calculated by subtraction of the final mass of the sponge m<sub>f</sub> from the initial mass m<sub>i</sub>). In this study the sponge was placed underneath the stone sample and the sample was pressed from above against the contact sponge, thus causing the water to be adsorbed by upwards capillary forces, similarly to the capillary rise measurements.

#### 2.2.4. Mirowski pipe (MIR)

The Mirowski pipe has been developed and patented by the Polish Prof. Ryszard Mirowski (Patent No 125504). The method consists of a graded glass tube, closed at the top and with a small cylindrical body containing a sponge on the other end (Fig.1d). The gradations reach from 0 to 10 ml, divided in sub-gradations of 0.1 ml. For the measurement with MIR, the pipe is filled with water through the open cylindrical body, after which it is closed by adding the small sponge in the cylindrical body to prevent water from escaping the pipe. To attach the tube to the surface under analysis, a partially open rubber ring with two metal pins is fixed to the surface with tape above the designated measuring point. The filled pipe is then placed in the rubber ring, as such that the sponge touches the measuring point. Water is adsorbed by the stone through the sponge by capillary forces. According to the manual of MIR, the amount of water adsorbed can be recorded by measuring the reduction of the water volume in the graded pipe. Preliminary tests by the author [23] showed that when water is

adsorbed, air enters the tube, but in most cases the air bubbles stay trapped into the sponge instead of rising to the top of the tube and thus lowering the water level. As a consequence, the water uptake at a certain contact time could not be recorded correctly. Only at the moment when the tube is released from the surface, most air bubbles do start rising. To bypass this practical inconvenience, a modification was made to the protocol. The tube was weighed before measurement and after each designated period of contact with the stone, allowing calculation of the WAB according to Eq. (1), where A equals the surface of the Mirowski sponge (0.000113 m<sup>2</sup>);  $\Delta m$  the amount of water adsorbed from the pipe (calculated by subtraction of the final mass of the pipe m<sub>f</sub> from the initial mass m<sub>i</sub>). In accordance to the recommendations for KT, the WAB between the 5th and 15th minute was also calculated with Eq. (2).



Fig. 1. Illustration of the methods under study: (a) Capillary rise method (UNI/NORMAL 10859); (b) Karsten tube; (c) Contact-sponge method; (d) Mirowski pipe.

## 2.2.5. X-ray radiography

X-ray radiography and tomography have become important techniques of investigation in different fields, including soil science and fluid-flow research [24]. In this study X-ray radiography was used to visualize the water adsorption process inside stone samples of the lithotypes MC, MJ, V and E. X-ray radiography was performed at the Centre for X-ray Tomography at Ghent University (UGCT, Ghent, Belgium), with a micro CT scanner with an open type Feinfocus tube [25]. An energy around 80 keV was installed. As detector, a PerkinElmer XRD 1620 CN3 was used. The samples (dried until their constant dry mass was reached and cooled down to room temperature) were positioned between the source and detector and time lapse radiographs with a predefined time interval were taken. To improve the visualization of the water, the images of the adsorption process could be observed objectively through changes in grey values and quantified by measuring the height of the waterfront in function of time.

#### 3. Results and discussion

Besides the non-destructive methods KT, CSM and MIR, CR was also included in this study, as a reference method for the analysis of the WAB. In a first stage all methods were preliminary tested by the operator to gain familiarity with the application and to examine the possibilities and limitations of the methods. In a second stage the performance of the methods was scrutinized by analysing the relation between the open porosity and WAB measured by each method (1), comparing the performance of different methods with the normalized CR (2) and studying the influence of variable factors (3). Table 2 gives an overview of the average WAB and variation coefficient measured with the different methods on seven lithotypes. To have a comparable basis, two specific contact times for the measurements were predefined, based on the provided application standards or manuals of the methods. For all methods a contact time of 90 sec was applied. For KT and MIR the WAB between the 5th and the 15th min was also measured, according to the RILEM II.4 recommendations [21]. For each lithotype the average WAB was calculated on 16 samples for CR, CSM, KT and on 5 samples for MIR. It has to be mentioned that the WAB for KT is 10 times lower in comparison with earlier published results [15], due to a miscalculation in previous results. This miscalculation has been corrected in Table 2. The WAB of KT  $\Delta$ 5-15 min for the stones T and E cannot be taken into account as in most cases all water from the pipe was adsorbed before the 15 min had elapsed and the pipe was not refilled during measurement. Therefore, no valid results were obtained for these stones.

Table 2. Average open porosity [%] and WAB (average  $[g/m^2s] \pm$  standard deviation and variation coefficient [%]) for seven lithotypes. For each stone type the average was calculated on 16 samples for CR, CSM, KT and on 5 samples for MIR.

	OP	CR 90s		CSM 90s		KT 90s		KT Δ5-15 min		MIR 90s		MIR $\Delta 5-15 \min$	
MC	10.7	2.3±0.2	7.9	2.7±0.2	7.3	1.6±0.5	30.8	0.8±0.2	22.0	5.0±1.3	25.6	$1.6 \pm 1.0$	62.5
MJ	10.5	2.8±0.6	20.7	3.0±0.8	27.7	1.8±0.7	38.3	0.8±0.3	34.9	7.4±4.7	63.4	1.7±1.4	81.5
S	10.6	2.9±0.4	13.3	$3.3 \pm 0.4$	11.5	1.5±0.5	32.8	1.2±0.3	23.1	5.5±2.0	36.1	2.1±0.6	28.7
V	13.5	2.8±0.2	8.0	3.7±0.3	8.1	1.6±0.6	35.7	1.1±0.3	28.0	8.4±6.3	74.3	3.5±1.5	42.9
Μ	15.6	5.4±1.5	28.2	5.8±1.5	25.9	3.8±2.6	67.6	1.6±0.9	58.6	5.8±3.4	58.7	3.2±2.0	38.0
Т	23.7	13.2±1.8	13.8	19.4±1.7	8.8	13.5±2.4	17.9	-	-	32.3±2.1	6.6	16.8±6.4	38.0
E	29.3	31.7±5.0	15.7	30.6±3.2	10.5	29.7±9.8	33.1	-	-	44.3±11.9	26.8	27.3±8.6	31.5

When comparing the values for the WAB with the open porosity, one of the physical properties of the stone determining the WAB, a similar trend between the WAB and the open porosity can be observed for all methods. The higher the open porosity, the higher the adsorption values. Although all methods follow the same trend, the absolute values differ in each method. When compared to the standardised CR, it can be noticed that CSM shows slightly higher adsorption values, KT measures a lower WAB and MIR 90s a much higher WAB. As measurements were performed in identical conditions on identical materials, the reason for these discrepancies has to be found by the differences in practical application and design of the methods.

When considering the practical application, each method encounters a number of limitations and/or encumbrances. For CSM the amount of available water is limited by the content of the sponge. In case of examination of more porous stones, the amount of water in the sponge can be insufficient to supply for the WAB of the stone. Previous research on water transport between contact material and stone structure by means of X-ray radiography at UGCT Ghent clearly illustrated this limitation and led to the adaptation of the application procedure for CSM [23]. This limitation also explains why the result for E with CSM is lower than with CR, which is in contrast with the results for the other lithotypes. KT suffers two hindrances, namely the contact area not being constant and the adsorption of water before the actual start of the measurement. To obtain sufficient adhesion and a watertight sealing plastiline is used, which is pressed between the stone and the tube, causing the plastiline to expand sidewards, reducing the contact area irregularly and consequently lowering the admittance of water to the stone surface. Measurements with KT only start once the water level reaches the zero gradation on de graded tube. Water being adsorbed while pouring water in the tube is consequently not taken in account in the

measurement, which could cause a lower WAB. MIR on the other hand suffers of frequent leaking. As the contact area of MIR is rather small, the quantitative water uptake is very low and only a small leak is sufficient to cause a considerable deformation of the calculated WAB. The impact of these practical encumbrances is reflected by the variation coefficients (Table 2). For CSM and CR the variation coefficient is of the same acceptable magnitude, whereas for KT and especially MIR the variation coefficient is almost unacceptably high. All limitations and possibilities of the methods were considered in detail in previous research [26]. It was concluded from this research that CSM is capable of measuring the initial water uptake of less porous materials with a high precision, but is not suitable for analysis of longer measuring periods of more porous stones. KT was found incommodious for measurements of the water uptake before 5 minutes, but it has the possibility of measuring longer contact times for more porous lithotypes. MIR showed too many discommodities, leading to unreliable results.

When considering the design, a number of factors are not equal for each method, namely the size of the contact area, the contact material and the pressure applied by the water on the surface. To analyse the influence of the contact area, an additional series of tests was made, where the WAB by capillary rise (DIN 52617) was measured on samples where the surface in contact with the water was taped corresponding to the respective contact areas of the different methods (Fig. 2). Ergo, as in all cases the CR method was applied, the influence of the pressure and contact material on the measurements could be excluded. It has to be mentioned that only three samples per test case were analysed, so that clear trends can be derived reliably from these tests, whereas exceptions have no statistic value. Fig. 3 shows the capillary adsorption curves of the above described experiments on the lithotypes MJ, MC, V and E. The curves CR CSM, CR KT and CR MIR depict the capillary water uptake in function of time (following DIN 52617 procedure) with contact areas taped corresponding to the different standardised application procedures, namely DIN 52617 (CR G) and UNI/NORMAL 10859 (CR F). CSM, KT, MIR, CR are the results of table 2 which were included the graphs.



Fig. 2. Surface of the stone samples under investigation, taped according to the respective contact areas of the methods: Contact-sponge method, Karsten tube and Mirowski pipe.

When considering the effect of the size of the contact area, for all lithotypes a clear relation can be observed between the water adsorption and the size of the contact area  $(g/m^2)$  in function of time: the smaller the contact area, the higher the WAB when calculated according to Eq. (1). This is most probably caused by the additional sidewards adsorption of the pores surrounding the contact area. For CR the total surface of the sample is brought in contact with water, impeding additional sidewards adsorption. For the other methods with a restricted contact area in comparison to the sample under investigation, pores on the borders of the contact area adsorb additional water. The smaller the contact area, the more pores are surrounding the contact area relative to the contact area itself. So more additional water can be adsorbed sidewards in relation to the water adsorbed by the contact area itself. This occurrence was confirmed by visualization of the water adsorption by the different methods by X-ray and neutron radiography [26]. From these experiments it can be concluded that the calculation method as proposed in Eq. (1) is not convenient for comparison of the WAB measured by different techniques having various contact areas. A study of physico-mathematical models for calculation of the water adsorption where the sidewards adsorption is taken in account, such as the model of Wendler and Snethlage [27], is currently ongoing.



Fig. 3. Capillary Rise measurements on lithotypes MJ, MC, V and E. Curves CR CSM, CR KT, CR MIR are the result of measurements on samples where the surface in contact with the water was taped, corresponding to the respective contact areas of the different methods. Curves CR G and CR F compare Capillary Rise measurements according to application procedures DIN 52617 and UNI/NORMAL 10859 respectively. CSM, MIR, CR and KT are the results of the different methods of table 2.

In order to study the influence of the pressure and the contact material, the results of table 2 were included in the graphs in Fig. 3. The curves CR CSM, CR KT and CR MIR represent the capillary water adsorption curve for each method in case of an unhindered water supply, whereas CSM, KT, MIR, CR represent the water adsorption by the different methods. From this comparison it can be noticed that CSM reveals a slightly lower adsorption than CR CSM. For less porous stones the difference is smaller and falls within the standard deviation, whereas for the more porous stones the discrepancy exceeds the standard deviation. This dissimilarity for more porous stones is probably due to the limited amount of water in the sponge or could indicate a probable hindrance by the contact material. KT exhibits a much lower adsorption than CR KT, albeit the difference is almost constant for the different contact times. This is most probably the effect of the contact area not being constant and the adsorption of water before the actual start of the measurement, as mentioned above. MIR shows no clear trend in comparison with CR MIR. Taking in account the high variation coefficient of the method and the fact that only three samples were analysed, no conclusion of statistical value can be drawn, except a confirmation of the unreliability of the method.

For analysis of the influence of the contact material, both standardised application procedures for CR, namely UNI/NORMAL 10859 (CR F) and DIN 52617 (CR G) were compared for all seven lithotypes under study (Table 1). Analysis of Variance (One-way ANOVA) of the results indicated no significant differences between both methods with a probability of 95%. This indicates that the contact material has no significant influence on the WAB of the lithotypes under study.

A third variable factor of the methods is the pressure applied by the water on the stone surface. CR and CSM do not exert any pressure on the surface, as the water supply is not sealed to the stone sample. In case of pressure, water will escape out of the system instead of being pressed into the stones' capillaries. For KT water exerts a pressure on the stone surface of 961.38 Pa, due to the water column with a height of 9.8 cm. When water is adsorbed, the water level lowers, along with the pressure. As the tube is sealed to the surface, the water will indeed apply this pressure on the stones' capillaries. In case of MIR the graded tube is closed at the top and water can only escape from the tube through the sponge if air can enter the tube through that same sponge. As a consequence, this practical inconvenience causes an under pressure does not seem to have a major influence on the measurement in comparison with the influence of the size of the contact area for the lithotypes under study. According to Klopfer [28] pressure can influence the depth of penetration, depending on the pore size distribution of the lithotype. This influence will be further studied by investigation of the pore size distribution of the lithotypes under study in combination with neutron radiography.

When considering the variable factors of the methods due to their design, it is found that the size of the contact area is the most decisive parameter influencing the measurements when the WAB is calculated according to Eq. (1), whereas differences in contact material and pressure are situated mostly within the range of the standard deviation and do not exhibit a significant influence. As the number of samples under investigation was limited, these conclusions have to be considered as preliminary results, which will be further investigated by means of X-ray and neutron radiography.

#### 4. Conclusions

The performance of various non-destructive techniques for measuring the WAB, namely the Contact-sponge method (CSM), Karsten tube (KT) and Mirowski pipe (MIR), was studied with the focus on an adequate comparison of the measurements correlated to the methodologies of the methods. Therefore, the accuracy of the methods was tested in relation to the open porosity of seven lithotypes with a varying open porosity and compared with the results of the normalized Capillary rise method (CR). Furthermore, practical encumbrances which could confine the application of the methods were examined as well as the influence of variable factors due to the specific design of the methods. The general conclusion is that the results of the different methods are related and provide a relation with the open porosity. Concerning limitations in practical application it is noticed

that CSM and KT have complementary fields of investigation, where CSM is capable of measuring the initial water uptake of less porous materials with a high precision, but is not suitable for analysis of longer measuring periods and/or of more porous stones, due to the limited amount of water in the sponge. KT was found incommodious for measurements of the water uptake before 5 minutes, but it has the possibility of measuring longer contact times for more porous stones. MIR showed too many discommodities, leading to unreliable results. When considering the variable factors of the methods, it can be concluded that the size of the contact area is the most decisive parameter influencing the measurements when calculated with the current formula, as pores surrounding the contact area cause an additional sidewards adsorption. Differences in contact material did not exhibit a significant influence. These conclusions are currently being further investigated by means of X-ray and neutron radiography in combination with a study of physico-mathematical models describing the WAB.

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