Gel structure of the corrosion layer on cladding pipes of nuclear fuel

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ABSTRACT

The fuel material in a nuclear reactor is protected by cladding pipes made of alloyed zirconium. In contact with water near its critical temperature, a corrosion layer of hydrated zirconium dioxide $ZrO_2 \cdot nH_2O$, probably with an amorphous gel structure under given conditions, is formed on the cladding. To verify the presence of the gel structure, an analysis was made by water vapour desorption of the original corrosion oxide layers stored in a given autoclave liquid, their dehydrated modifications, and modifications rehydrated in an aqueous medium. This analysis enabled the varying water content to be determined as a characteristic quantity reflecting the nature of its binding. Microhardness values as a measure of plastic deformation of the crystalline and amorphous forms of zirconium dioxide were also determined. Unambiguous agreement of the results obtained by sorption analysis and by microhardness measurement allows us to conclude that the corrosion layer in situ has properties corresponding to a reversible xerogel.

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1. Introduction

Requirements for economical and safe operation of nuclear power plants have been reflected in increased demands on cladding pipes of fuel elements, which are the first barrier preventing the release of fission products into the reactor coolant. These cladding pipes are made of zirconium alloys of various chemical compositions, various content of alloying and trace elements, and various production technologies. Although zirconium alloys are highly resistant, a corrosion layer of zirconium dioxide is formed on the surface of these pipes under the thermodynamic conditions in a reactor [1]. In view of the fact that this corrosion is a factor that limits the burnup of nuclear fuel, there is a general effort to reach a precise understanding of the corrosion mechanism, leading to a detailed study of this problem.

In the Czech Republic, the properties of the corrosion layer and the corrosion kinetics are studied in long-term corrosion tests in the laboratories of UJP Praha Inc. [2,3]. One of the methods applied in identifying the properties of the corrosion layer is water vapour sorption, which is suitable for special analysis of solid surfaces thanks to its extraordinary properties [4]. These properties are the size of a water molecule, with a kinetic diameter of about 0.3 nm, allowing it to enter the smallest micropores, and its polar character, allowing selective interactions with surfaces of different chemical composition. The simplest manifestation of this interaction is the distinction of hydrophilic and hydrophobic surfaces. From the shapes of the adsorption and desorption branches of the isotherm and their mutual position, conclusions can be drawn

on the sorption in outer surface layers or on the surface of coarse pores without capillary condensation, on the presence of micropores, or on the water chemisorption. Anomalous behaviour was observed for samples, after autoclave exposition dried at 80 °C and being stored in air [5]. In these samples, a larger amount of gas or vapour was released than the adsorbed amount, due to adsorption of airborne carbon dioxide. The evaluation of a corrosion layer can be affected by pressure and temperature conditions, upon which the analysis is performed and which differ from the conditions present at the origin of such layer. It cannot be reliably assumed that a layer of ZrO_2 chemical composition will have identical properties at 360 °C and corresponding pressure as in tests carried out at a temperature of about 25 °C and barometric pressure, or in vacuum. Loss of water present in the layer and any modification of the layer during its exposition to air before analysis are of the greatest importance. The change in medium will probably not be reflected in a chemical analysis of the layer, however, its structure and some physical and mechanical properties will certainly be affected. In the crystalline part of the hydrated layer, XRD analysis revealed systematic differences in residual strains, crystallite sizes, and microdeformations in samples after water loss, compared to samples with the original water content [6].

It is known that ZrO_2, similarly to other oxides of the 4th subgroup of the periodic table, e.g., TiO_2, SiO_2, GeO_2, and SnO_2, is gradually hydrated forming hydrated oxide of a gel character [7], when exposed to water. This process is reversible, and in the course of aging the hydrated oxides are transferred from the gel form back into the crystalline form, which can be unambiguously proven by XRD, contrary to the amorphous gel form. In the form of a gel, hydrated oxides retain water by sorption and capillary forces. The gel

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represents a two-phase system forming a joint structure composed of solid and liquid components, resp. disperse phase and disperse medium [8]. The disperse phase is formed by the hydrated crystalline oxide, and the disperse medium is water.

The present study has been aimed at identifying the transition of the hydrated crystalline form $ZrO_2 \cdot nH_2O$ into a gel in the form of a disperse phase. Evidence of the gel form existence has been based on different water content in the gel and in the crystalline oxide. As the most precise method for determining content of water and its binding mode, the desorption branch of the water vapour isotherm was chosen. Microhardness testing was applied to determine the effect of close participation of solid and liquid components in the properties of the joint structure in the two-phase system of the gel, in comparison with the single-phase system (crystalline oxide) [9]. This procedure was realised using the basic property of the gel, assuming that the continuous net-like structure of zirconium dioxide as the disperse phase remains preserved when the sample is converted to the anhydrous state. On the other hand, loss of water after drying the corrosion layer is a factor disturbing its gel properties obtained in situ, and thus also the necessary continuity of the disperse medium. For this reason, samples tested within this study were stored in a liquid.

2. Experimental

2.1. Oxidation

Cladding pipe samples made of ZrNbSnFe, IMPZry-4, and Zry-4-standard alloys have been tested [10]. Their outer diameter was 9.8 mm, wall thickness 0.64 mm, and length 30 mm. An opening 3 mm in diameter was made in the samples in order to hang them in an autoclave, and also to hang them on a thin tungsten wire connected with the sorption microscale beam during the sorption analysis. Before oxidation, the samples were polished mechanically and degreased in an ultrasound bath in an ethanol–acetone (1:1) solution. The isothermal corrosion tests were carried out under static conditions in a pressurized autoclave according to ASTM-G2M88 (re-approved in 1996) in demineralized and deionized water, at temperature 360 °C and pressure ~19 MPa, with exposition times up to 84 days. After exposition, wet samples taken from the autoclave were transferred into a vessel filled with the actual autoclave liquid. In this state in the closed vessel they were left to cool down and stored until analysis. The volume of this protecting bath was sufficient to ensure permanent complete immersion of the corrosion layer during the entire manipulation with the vessel.

2.2. Methods

The sorption experiments were carried out using an IGA 002 (Intelligent Gravimetric Analyser) by HIDEN (UK) designed for gravimetric measurement of both gas and vapour sorption and allowing determination of the water vapour adsorption and desorption isotherms for preset pressure steps [11]. The instrument can be operated manually or by a computer, according to the selected program. Changes in weight are indicated by a two-beam balance with a sensitivity of 10^{-7} g. In the course of the sorption process, sample temperature was automatically controlled within the range of ±0.05 °C and the pressure converter that was used worked with accuracy ±0.02%. Approaching the equilibrium state was analyzed in time, and the weight change was recorded upon reaching 98% of an asymptotic value according to a computer algorithm. Evacuation of the sample and of the inner space of the instrument was realised by a membrane pump at the first level, and by a turbomolecular pump capable of reaching 10^{-4} Pa vacuum at the second level.

After evacuation of the samples studied until a constant weight at 25 °C, 15-point water vapour desorption and adsorption isotherms were measured at 25 °C at pressures ranging from the saturated pressure of 3.2 kPa until 0 kPa, and from 0 to 3.2 kPa, respectively. The weight decrease/increase at each pressure point were measured under isothermal conditions until attaining equilibrium. After the equilibrium was established, the vapour pressure was decreased to the next preset pressure value and the subsequent decrement was measured until the equilibrium was reestablished. The process was repeated until the desorption data points required for the isotherm were obtained. In the case of adsorption, a reverse procedure was carried out.

Microhardness was determined at 25× magnification using an Amplival microscope with a dry objective, equipped with a diamond pyramid for microhardness determination by the Vickers method. Microhardness was measured at 24 points on the pipe surface (eight times lengthwise and three times breadthwise) and expressed as (MH) (GPa).

2.3. Experimental procedure

The content of water as the disperse medium and microhardness as a characteristic of the gel structure was determined at 25 °C for the original samples exposed in an autoclave and two modifications derived from them. First, Vickers microhardness was determined for an original sample taken from the autoclave (MH1), and then, after removing free water by evacuation, the desorption branch of the water vapour isotherm (DES1) was measured until complete dehydration of the gel up to it's disperse phase.

For this disperse phase as the first modification derived from the gel, the weight of this corrosion layer covering the entire cladding pipe was determined (DP), and both branches of the water vapour isotherm were measured (ADS1/DES2) to document the extent of interaction of zirconium dioxide with water molecules. The microhardness of this sample was determined both at the initial point of the isotherm (MH0), where it corresponds to the hardness of the disperse phase alone, and at the point corresponding to the saturated pressure of water vapour (MH32).

After following desorption up to the anhydrous state, the recovered disperse phase was placed into boiling water for 48 h to ensure its transition into the gel form, and thus also its reversible xerogel character. For a sample obtained this way, which represents the second gel modification, the microhardness (MH3) and the desorption branch of the water vapour isotherm (DES3) were again measured.

2.3.1. Sorption analysis procedure

For the samples exposed in an autoclave as well the samples hydrated in a water bath, the surface free water was wiped away using a fine absorbent paper after withdrawal from the protective bath. Their total ballast water was removed in the sorption analyser by evacuation up to the water vapour saturated pressure. To prevent disturbing the presence of water in the gel structure after the pressure decrease to 3.2 kPa during evacuation of the analyser instrument at 25 °C, several drops of free water were added into the sorption cylinder with the sample hung on the microscale beam. Unlike the water in a gel, the evaporation of these added water drops was not affected by any force interaction with the surrounding medium. This preferentially ensured the atmosphere of water vapour in the sorption cylinder at the saturated pressure, thus preceding water evaporation from the gel. This stage of evacuation was controlled manually, and if the pressure in the cylinder decreased below 3.2 kPa by more than 1 Pa, evacuation was repeatedly interrupted for the necessary time of several seconds until the controlled pressure value was restored. If the pressure
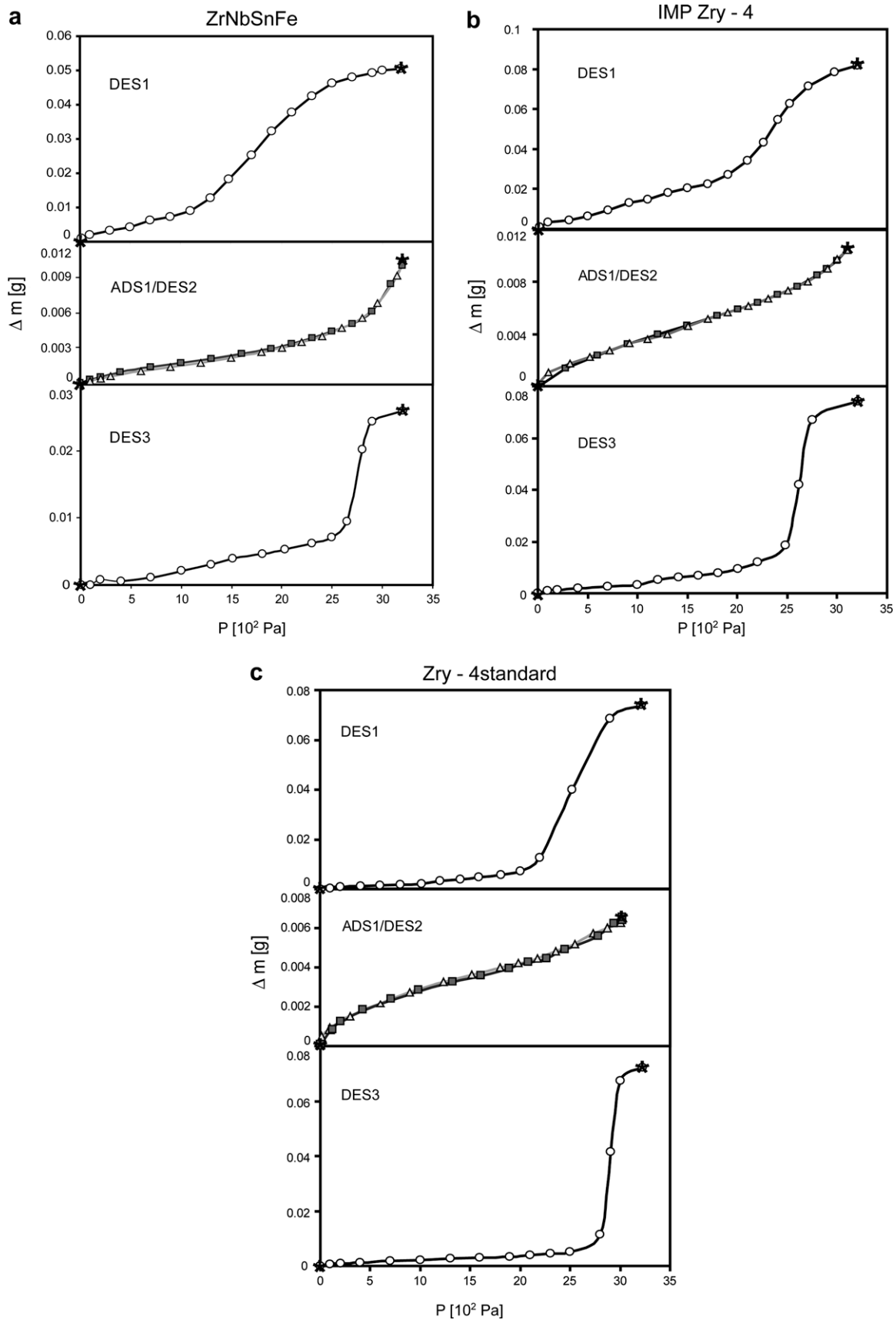
Fig. 1. Sorption isotherms of water vapour at 25 °C on zirconium alloys: (a) ZrNbSnFe, (b) IMP Zry-4, (c) Zry-4 standard (DES1 – desorption branch for the original corrosion layer obtained in autoclave, ADS1/DES2 – adsorption/desorption cycle on anhydrous sample, DES3 – desorption branch for the dry layer rehydrated by water bath at 100 °C; asterisk on the isotherm marks point with determined microhardness).

decrease was not balanced backward after this time, it indicated that free water evaporation had come to an end.

Subsequent desorption of water from the gel was again controlled by the computer, with a programme covering the whole pressure range of desorption from 3.2 to 0 kPa. As soon as desorption approached a minimum pressure close to zero, it was terminated and followed by evacuation of the sample at a temperature below 25 °C only to prevent possible thermal alteration of the textural and/or chemical character of the corrosion layer.

For a desorbed anhydrous sample exposed in an autoclave, the standard adsorption/desorption cycle was measured at 25 °C within the pressure range 0–3.2 kPa.

3. Results and discussion

The results of the sorption analysis carried out for three oxidized samples of cladding pipes made of various zirconium alloys are illustrated in Fig. 1a–c, which depict the desorption branches of the water vapour sorption isotherm (DES1) in an original corrosion layer obtained from the autoclave, the isotherms of the subsequent adsorption/desorption cycle (ADS1/DES2), and the desorption branches (DES3) for the anhydrous layer rehydrated in a water bath.

The shape of both desorption branches (DES1) and (DES3) is quite similar. However, between pressures of about 15 and 32×10^2 Pa, the decrease in the (DES1) branch is slower than the steeper decrease of (DES3). Such shapes are typical for corrosion layers in all samples made of different alloys. A possible explanation is that during preparation of the corrosion layer in the autoclave, the water molecules in the gel formed a stronger bond, which was broken during desorption only at a suitable lower pressure and thus influenced the rate of desorption from the gel.

Co-occurrence of the corrosion layer and water as the disperse phase and disperse medium, respectively, within the gel are a characteristic signature of its internal arrangement. With respect to the spatial discontinuity of the anhydrous corrosion layer in the form of the crosslinked dispersion phase, as follows from the micrograph in Fig. 2 [12,13], the abundance of both disperse components within the gel was expressed by their relative volumes, which respect the structural similarity of xerogel according to water sorption. The total desorbed amount of water (WD1) according to (DES1), expressed as a relative volume fraction of the disperse

medium in the layer, is very similar in all samples, about 50 vol.%, as well as the volume fraction of zirconium dioxide as the disperse phase. The total amounts of desorbed water (WD3) according to (DES3) are lower only in sample ZrNbSnFe. For comparison, the amount of water bound in the corrosion layer at the saturated pressure (WAD), which is always significantly lower than amounts (WD1) and (WD3) was subtracted from the reversible adsorption cycle ((ADS1/DES2), see Fig. 1). The reversible character of the adsorption/desorption indicates that sorption occurs on a nonporous surface only, at most in macropores, which can be classified as a part of the variability of the gel disperse phase. The respective values together with other ones are presented in Table 1.

The significance of the water contents determined in the original samples and their two modifications in connection with the structural arrangement of corrosion layers was also confirmed by
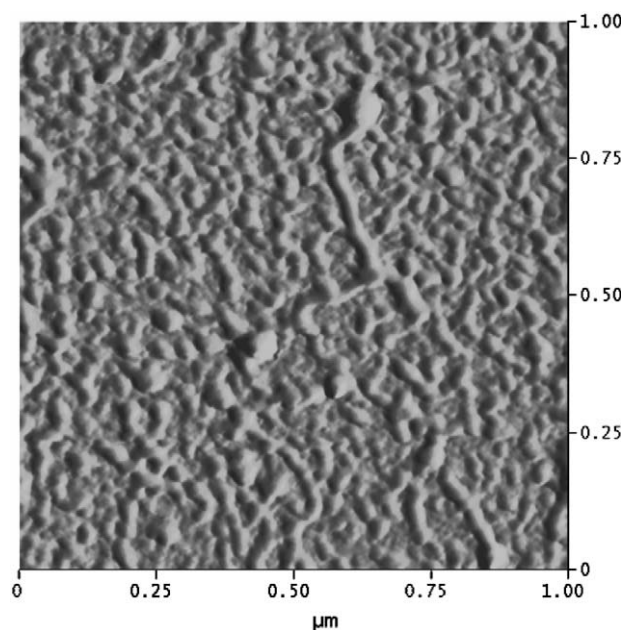

Fig. 2. AFM image illustrating the surface morphology of the anhydrous corrosion layer as crosslinked dispersion phase (nanoscope IIIa multimode microscope).

Table 1
Results of sorption analyses and microhardness measurements for three modifications of the gel components.

Parameter	Alloy		
	ZrNbSnFe	IMPZry-4	Zry-4 standard
Mass of disperse phase (DP) (g)	0.3106	0.4357	0.4309
Volume of disperse phase* (VDP) (cm³)	0.0542	0.0760	0.0752
Microhardness of disperse phase (MHDP = MH0) (GPa)	4.45	4.46	4.29
DES 1 (25 °C) desorption of the corrosion layer hydrated in autoclave			
Conditions of layer preparation medium/temperature/time	water/360 °C/ 70 days	water/360 °C/63 days	water/360 °C/84 days
Amount of desorbed water (WD1) (g)	0.0492	0.0820	0.0741
Microhardness of gel layer (MH1) (GPa)	3.12	2.51	2.58
Volume ratio of components (WD1)/(VDP) (%vol)	47.6 / 52.4	51.9 / 48.1	49.6 / 50.4
ADS/DES 2 (25 °C) adsorption/desorption cycle onto disperse phase			
Amount of desorbed water (WAD) (g)	0.0103	0.0123	0.0076
Microhardness at pressure 0 mbar (MH0) (GPa)	4.45	4.46	4.29
Microhardness at pressure 32 mbar (MH32) (GPa)	4.33	4.45	4.13
Volume ratio of components (WAD)/(VDP) (%vol)	15.3 / 84.3	12.9 / 87.1	9.5 / 90.5
DES 1 (25 °C) desorption of the corrosion layer hydrated in water bath			
Conditions of layer preparation medium/temperature/time	water/100 °C/ 48 h	water/100 °C/ 48 h	water/100 °C/ 48 h
Amount of desorbed water (WD3) (g)	0.0252	0.0744	0.0702
Microhardness of gel layer (MH3) (GPa)	2.70	2.30	2.20
Volume ratio of components (WD3)/(VDP) (%vol)	32.6 / 67.2	49.5 / 50.5	48.1 / 51.8

* (VDP) = (DP)/d, d = 5.73 g/cm³ (density of ZrO_2).

the microhardness values (MH). This justifies the application of microhardness as a characteristic analytical parameter. While crystalline zirconium dioxide shows higher deformation resistance against indentor penetration, and thus higher Vickers microhardness (MH) as a measure of plastic deformation, for the gel as a homogeneous volume mixture of zirconium dioxide and water, it must be expected that its plastic deformation is affected by the deformation properties of both components, which is reflected in lower deformation resistance during indentation, and thus also a lower (MH) value [14]. The points at which microhardness was measured within the sorption analysis are marked with asterisks in the graphs of Fig. 1a–c, and the respective (MH) values are listed in Table 1. From the position of the points and the corresponding values (MH1, MH3), it is evident that microhardness very well distinguishes the actual state of the corrosion layer in the form of a gel or xerogel. It follows from the virtually equal values (MH0) and (MH32) that they relate to identical material, the disperse phase in this case, thus no structural transformation occurred during adsorption.

4. Conclusion

The principal results are as follows:

1. As follows from the second desorption (DES3), repeated contact of the anhydrous disperse phase with water causes absorption of a water amount (WD3) comparable with the water amount (WD1) released at the first desorption (DES1).
2. From a comparison of the water amounts (WD1) or (WD3) according to the desorption branches (DES1) and (DES3), respectively, with the substantially lower water amount (WAD) according to the sorption cycle (ADS1/DES2), it follows that in the former case water supplements the present zirconium dioxide as a disperse medium within the gel, whereas in the latter case it is only the water adsorbed on the surface of zirconium dioxide.
3. These relations have been confirmed by microhardness values (MH). The original water-containing samples had lower (MH) values before desorption (DES1) or (DES3) and higher values after desorption, with the lower values characterizing the gel

with a higher degree of plastic deformation, and the higher values characterizing pure crystalline zirconium dioxide as a disperse phase with a lower degree of plastic deformation. From virtually identical (MH) values for the first and last points of the isotherm (ADS1/DES2), it follows that they relate to the disperse phase solely, and that no disperse medium has been formed.

It can be concluded on the basis of the above findings that the corrosion layer of zirconium dioxide has behaviour corresponding to a reversible xerogel.

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