MELCOR further development in the area of air ingress and the effect of nitriding

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ABSTRACT

It has long been recognized that overheated cladding undergoes exothermic oxidation in steam, leading also to generation of hydrogen. Under such circumstances the oxidation rate would typically be limited by the comparatively slow rate of oxygen diffusion through the oxide layer which builds up on the cladding surface. However, exposure to air can lead to accelerated oxidation since the effect of nitrogen degrades the oxide layer which hence becomes a less effective barrier, resulting in faster oxidation kinetics. The oxide layer typically becomes porous and can break away, a process known as breakaway oxidation. As well as faster oxidation, the nitrogen also promotes faster and more complete degradation of the cladding, leading to more widespread destruction of the fuel rods and exposure of the fuel itself.

Until recently it was believed that nitrogen did not play a major role as an active chemical species, instead its main effect was considered to be the accelerated oxidation. Recent experiments have shown that the reaction with nitrogen can result in extensive formation of zirconium nitride (ZrN) which contributes very significantly to both the heat generation and fuel rod degradation, in particular if the oxygen has already been sufficiently consumed.

The current project addresses the active roles of nitrogen and ZrN formation in the air oxidation modeling by means of a coupled analytical and experimental investigation. A nitriding model will be developed and formulated to be implementable into the reactor system analysis codes such as MELCOR and SCDAP.

Project goals

The goal of the project is an oxidation/nitriding model development which can be implemented into nuclear system analysis codes (e.g. MELCOR or SCDAP). In order to develop a nitriding model, the following steps are required:

- Thermodynamic analysis: This step focuses on understanding the nitriding process at the micro-scale. This is supported by analyses of the phase compositions within the zirconium-oxygen-nitrogen ternary system, based on available literature and thermodynamic data.
- Separate effect tests: Literature findings on the available separate effect tests; identify the main parameters that will be useful to develop a nitriding model. Perform series of independent separate effect tests to validate the proposed model.
- Kinetic analysis: Literature finding on the available data, identify missing data.
- Model development: Develop a nitriding model by integrating the observations of the thermodynamic analysis, the separate effect tests, and the kinetic analysis.

The present project is a coupled analytical and experimental work in the frame of PhD thesis work by Sanggil Park. Thus, the analytical work is performed at PSI under the supervision of Dr. Leticia Fernandez-Moguel and the experimental work is conducted at Karlsruhe Institute of Technology (KIT) being supervised by Dr. Martin Steinbrück.

Work carried out and results obtained

Air ingress scenarios are a concern for the nuclear industry. There are situations where air ingress scenarios may occur: during a severe accident the reactor pressure vessel could fail and air could ingress [1–2]; during mid loop operation when the reactor coolant system is usually opened to the containment [3] or in spent fuel facilities such as pools and dry casks in either the event of loss of cooling or handling and transport accidents [4–5]. Many separate effect tests have been performed in the past to study the influence of nitrogen effect during oxidation. The studies have mainly been performed with fresh Zircaloy-4 cladding samples; but also M5®, Zirlo™ and E-110 [6–12]. These tests have helped to reach a macroscopic understanding of the process. More recently, Lasserre et al. [13–14] have studied the degradation of Zircaloy-4 in an air environment at high temperatures considering a nucleation and growth model for nitrogen affected zones, but the understanding of the process was not progressed further since the role of nitrogen was taken into account as an auto-catalytic effect and the Zr-O-N ternary phases were not considered to understand the process.

The knowledge collected in the cited studies has helped to identify two major roles of nitrogen during air oxidation.

- Cladding degradation by forming a micro porous and macro cracked oxide due to the volume changes.
- Exothermic heat release from the nitride formation and reoxidation.

The current nitriding models employed in system analysis codes are still purely empirical and phenomenological. They are based on Zr-O binary system and partly on Zr-N binary system. Thus, only binary compounds, ZrO_2 and ZrN, are involved in a nitriding process. Besides, most of the current models miss several nitrogen effects (i.e. further cladding degradation by nitriding, exothermic heat releases from nitride formation and reoxidation, and hydrogen generation from nitride reoxidation by steam during reflood) as it was shown in the recent QUENCH air ingress experiment benchmark [15].

A PhD started in September 2013, in order to address the lack of knowledge on the nitriding effects. The goal of the thesis is to develop a nitriding model which could be implemented in nuclear reactor system analysis codes such as MELCOR. The PhD work plan for developing a nitriding model is shown in image 1.

For the first year of the PhD work, a survey of the literature and experimental data as well as thermodynamic analyses were performed. The study aimed to identify the nitriding process which may occur at a micro-scale level and that may not be observed in post-test examinations with conventional methods used in the nuclear field (e.g. Separate Effect Test).

Literature of the Zr-O-N system in the nuclear field is scarce, while Zr-O-N system has been studied for the application of electrical devices such as thin film in semiconductors [16] and fuel cell fabrication [17]. Based on these literature findings, the Zr-O-N ternary system thermodynamics, experimental data and Thermo-Calc calculations, possible mechanisms for oxidation in presence of nitrogen has been identified:

Image 1:
PhD thesis work plan
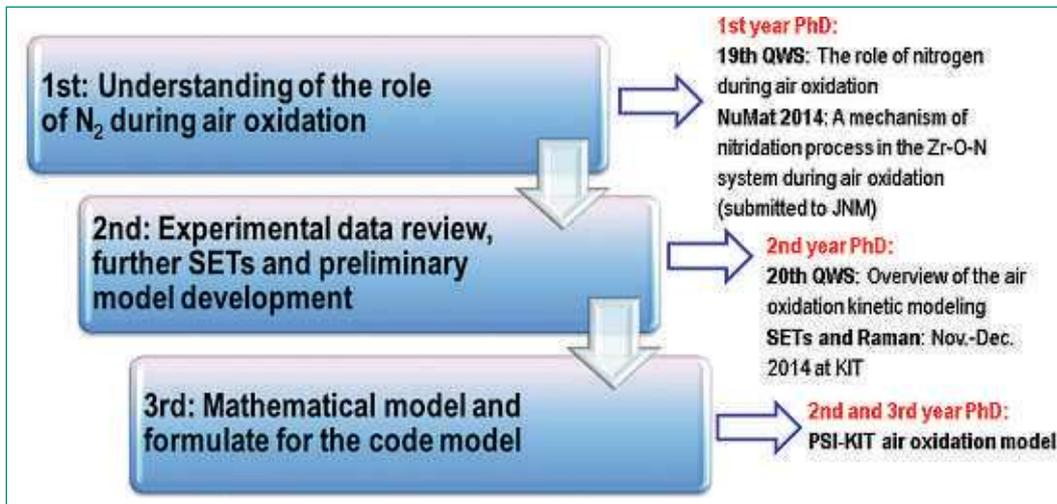
- The nitriding process begins from the metal-oxide interface by incorporating the nitrogen gas into the sub-stoichiometric oxide and the oxygen/nitrogen stabilized α-Zr. After solubility limits of the interfacial system have been exceeded, the ionic-covalent zirconium nitride, Zr_3N_4 is firstly formed.
- The Zr_3N_4 is in metastable state and thus it leads to oxide/nitride metastable system close to the interface.
- From the metastable system, nitrogen rich oxynitride phase of $γ-Zr_2ON_2$ is formed and then the nitrogen rich part of $Zr_3N_4/γ-Zr_2ON_2$ is developed near the interface.
- Above 800°C the $Zr_3N_4/γ-Zr_2ON_2$ is decomposed into ZrN, β-type zirconium oxynitrides and $m-ZrO_2$. However it should be noted that this hypothesis is based on literature studies. Currently, Raman investigation is ongoing in order to prove the existence of the mention components.
- Once the nitrogen gas is dissolved, the nitriding process becomes accelerated by the reaction between solid solution nitrogen and solid solution oxygen. Firstly, nitrogen gas should be dissociated and absorbed in either metal or oxide, because the activation energy of the nitrogen gas – metal (or oxide) is higher than that of nitrogen solid solution – oxygen solid solution.
- Provided oxygen is still available, all zirconium oxynitrides and ZrN are reoxidized by releasing the nitrogen gas which is available for further nitriding. Thus, the heterogenous Zr-O-N layer is finally oxidized to ZrO_2 by simultaneous nitriding-reoxidation process.

From the nitriding-reoxidation process, three main reactions are identified; solid-gas nitriding, solid solution nitriding and the reoxidation as shown in Image 2.

As shown in image 2, nitrogen gas is firstly incorporated (step 1); The incorporated nitrogen solution promoted the nitriding process (step 2) and then nitrogen is released (step 3) due to reoxidation of the nitrides.

The air oxidation process begins (step 1) from the pure Zr metal (or zirconium alloy). O_2/N_2 is dissolved by the metal forming α-Zr(O,N). When the solubility limit is reached oxide is formed. Near the oxide/metal interface a thin layer of $t-ZrO_2$ is formed, nitrogen is incorporated into the $t-ZrO_2$ at low oxygen partial pressure.

During step 2, the activation energy of the reaction decreases by the nitrogen solid solution. The incorporated nitrogen stabilizes the $c-ZrO_2$ from the $t-ZrO_2$ until the solubility limit (6%) of oxygen vacancies in the anion site of the $c-ZrO_2$. The nitride is firstly formed near the interface from the satu-
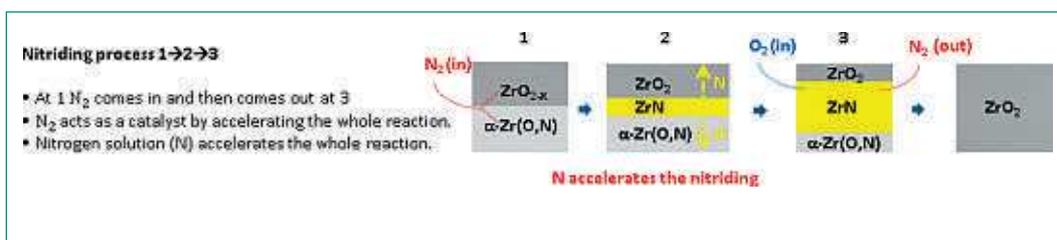
Image 2:
Schematics of the nitriding-reoxidation process

Start: Zr

Oxidation ①   O₂/N₂ dissolution

ZrO₂   Zr(O,N)

N₂ incorporation

Saturated c-ZrO₂   Saturated α-Zr(O,N)

② ③

Nitride formation

Self-sustained loop

pN₂/pO₂ in nitride stable region?   Y (further nitriding)

N

O₂ is sufficently available?   N

Y

Is fully oxidized?   Y

N ④

Reoxidation

Stop: self-sutained loop

Zr

N₂

ZrO₂₋ₓ
α-Zr(O,N)   O/M interface

ZrO₂
ZrN
α-Zr(O,N)

ZrO₂

Simple reaction equations
① Zr + O₂ = ZrO₂
② ZrO₂ + ⅖ N₂ = ZrN + O₂
③ Zr + ½ N₂ = ZrN*
④ ZrN + O₂ = ZrO₂ + ½ N₂

*Reaction ③, nitriding of Zr, is not with fresh Zr but with saturated α-Zr(O,N).

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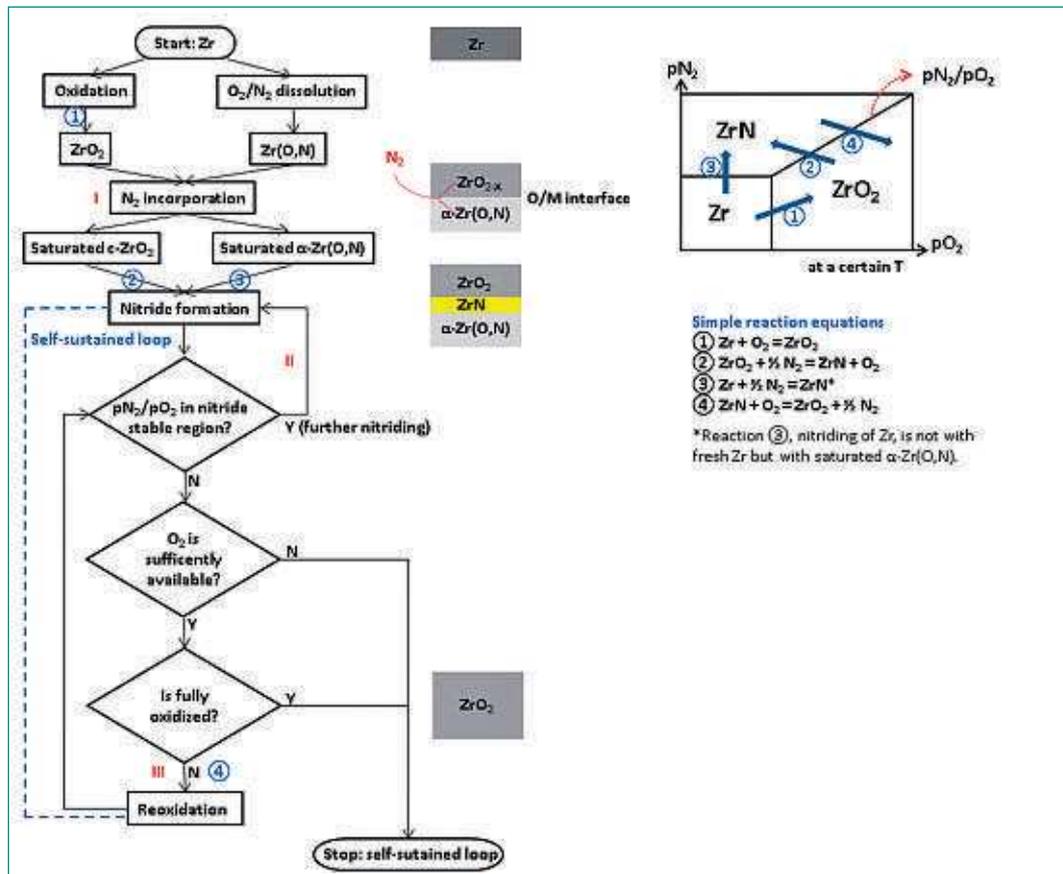
rated c-ZrO$_2$ and/or the saturated α-Zr(O,N). After the first nitriding formation, the nitriding process continues if the partial pressure ratio on the nitrogen/oxygen (pN$_2$/pO$_2$) is in the ZrN stable region. The nitrogen gas acts like a catalyst by accelerating the whole reaction. In reality, nitrogen is not a catalyst since it forms nitrides and oxynitrides.

However, if oxygen is newly available, the nitrides and oxynitrides are reoxidized and they would be transformed into zirconium oxide (step 3). Since the oxygen is a stronger oxidation agent than nitrogen, nitrides and oxynitrides are only stable at very low oxygen partial pressure [18]. This situation would be likely in spent fuel accident sequences, where nitrogen, oxygen and steam mixtures are likely.

Based on the collected information, a conceptual mechanism of nitriding process is proposed as shown in the flow chart (image 3). This will be the starting point for the model development.

During the nitriding-reoxidation process, in addition to the thermodynamic changes, there are mechanical changes associated to the phase transformations as shown in image 4.

From the nitriding, around 32% volume shrinkage has occurred and it would lead to micro porous and less coherent oxide scale. In other words, the protective oxide layer is degraded. Due to the micro porous nature of oxide scale, it is likely that if oxygen is available, it will easily diffuse through the degraded oxide scale and it will trigger reoxidation. From the reoxidation, zirconium oxynitrides and nitrides are decomposed and reoxidized with around 42% volume expansion.

Additionally, the oxide scale experiences local stresses and it leads to crackings by releasing the stresses. Thus, pores would be interconnected with grain boundaries and lateral cracks [19]. The coalescence of pores at grain boundaries and interconnection with the lateral cracks would result in the open diffusion pathway of the air [19–20] and it would gradually accelerate the reaction kinetics. N$_2$ is a product in the reoxidation process and it would be released from the reoxidized layer through the porous gaps, in that way it would be available for the further nitriding.

The nitriding-reoxidation may take place iteratively if oxygen is still available and self-sustained by the newly generated nitrogen until the whole scale is fully reoxidized to the ZrO$_2$. However, the self-sustained loop could be terminated if oxygen is unavailable or the cladding is fully oxidized.

The first year of the PhD work included the first theoretical approach which attempted to describe the detailed nitriding process by integrating Zr-O-N

literature studies, tests data, and thermodynamics calculations.

In summary, three possible mechanisms have been identified in order to explain the accelerated kinetics observed during oxidation in presence of nitrogen:

- Self-sustained nitriding-reoxidation process. Nitriding reaction is not significant in pure nitrogen environment with fresh Zirconium metal. However, nitrogen will play a role in mixed environments (i.e nitrogen/oxygen or nitrogen/steam) or when the Zirconium has been previously pre-oxidized. There are two possible locations were nitriding take place: Near the interphase and at the external oxide surface.

  – Nitriding is likely to occur near the oxide-metal interface at local oxygen starvation conditions. In this case nitrogen can react mainly with α-Zr(O,N) (i.e. the Zirconium metal has oxygen and nitrogen dissolved in it) and partly with Zirconium oxides.

  – Nitrogen can react with the external zirconium oxide surface only in case of nearly pure N_2 environment. Thus, nitrogen is incorporated to the surface oxide layer by forming the external nitride layer. Reoxidation is likely to happen when oxygen is sufficiently available to reoxidize the nitride and the nitriding is self-sustained by newly generated nitrogen during the reoxidation.

- Sudden kinetic transition. In the case of oxidation of fresh Zircaloy in the presence of nitrogen, first the oxygen should be consumed before the nitrogen can play any role. Oxygen and, to a minor degree, nitrogen are dissolved into the metal Zr, and after saturation some of the oxygen contributes to develop the oxide scale. The oxide scale is developed mainly by m-ZrO_2, but a small quantity t-ZrO_2 is formed close to the metal/oxide interface as a very thin layer [21]. The tetragonal phase is preferentially located near the interface by the following reasons [22]:
  – high compressive stress
  – low grain size
  – the presence of defects

If the volume-free energy difference between t-ZrO_2 to m-ZrO_2 becomes greater than the compressive strain energy at critical thickness, the t-ZrO_2 transforms to m-ZrO_2 with 4.56% molar volume expansion [23]. Once the oxide thickness exceeds the critical thickness, the stress built in this outer layer from the critical level does no longer sufficiently stabilize the t-ZrO_2 near the interface [24]. Thus, t-ZrO_2 transforms to the thermodynamically stable m-ZrO_2 near the interface. Because of the larger volume of the m-ZrO_2 than the t-ZrO_2, the m-ZrO_2 applies the emergent tensile stress to the underlying t-ZrO_2 and this tensile stress causes the cracks to be triggered. This crack tips propagate to the Zr/ZrO_2 interface as the oxidation proceeds due to the successive formation of the m-ZrO_2 at the crack tips [23]. Thus, the compressive stress is relieved at the free surface and hence the radial cracks initiate from the free surface toward the interface along the grain boundaries. Once the oxide layer is cracked, the gases could access easily to the oxide-metal interface through the radial cracks and it would lead to the sudden kinetic transition from the parabolic to accelerated linear kinetic rate. This phenomenon is delayed in pure oxygen/steam environment. However, in the presence of nitrogen, the sudden kinetic
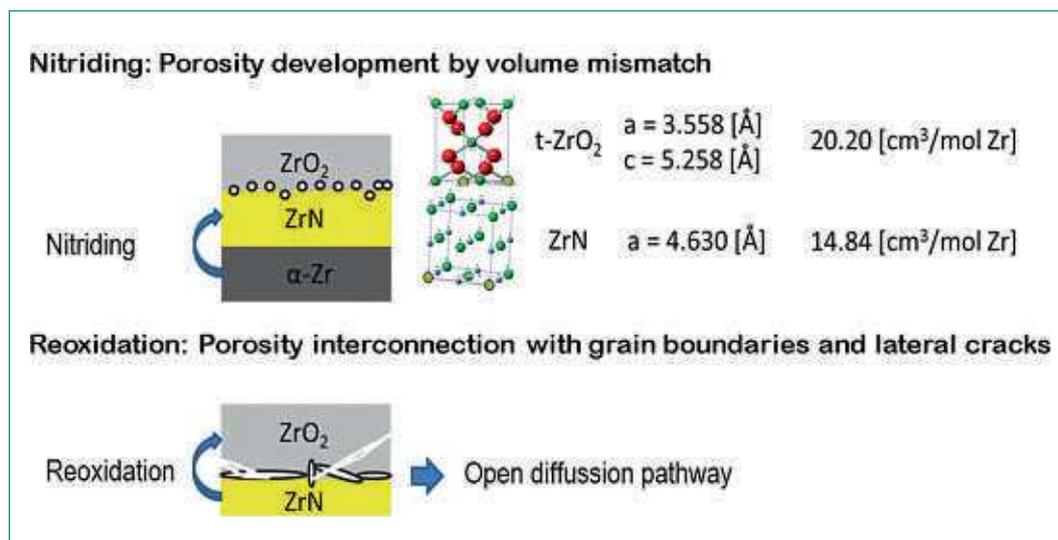
Image 4:
Mechanical changes during the nitriation-reoxidation process

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transition will take place earlier than in pure oxygen/steam environment due to the volume mismatches between nitride and oxide near the interface [10, 12]. The role of nitrogen on the kinetic transition is explained as a gradual kinetic transition.

- Gradual kinetic transition. During the self-sustained nitriding-reoxidation process, there are continuous phase transformations between the oxide and nitride. From the nitriding, pores are developed by volume shrinkage. On the other hand, these pores are interconnected during the reoxidation by volume expansion. The coalescence of pores at grain boundaries and interconnection with the lateral cracks would result in the open diffusion pathway of the air. Thus, the oxide has been progressively degraded by a porosity development and interconnection during the self-sustained nitriding-reoxidation process. This gradual kinetic transition may be the cause of the accelerated reaction kinetics.

The study forms a foundation on which to develop a nitriding model for nuclear reactor system analysis codes. For the second year of the PhD work, separate effect tests and Raman spectroscopy investigation will be performed at KIT in order to support the assumptions made in the present analysis and hence the nitriding model development.

National Cooperation

The student is enrolled at ETHZ and is supervised by Prof. Prasser/ETHZ.

International Cooperation

The PhD work is performed in collaboration with KIT. The PhD candidate had a first stay in KIT where he learned to perform thermodynamic calculations for the materials (Thermo-Calc. software) with a support from the KIT researchers. The first year of PhD work has been performed with frequent meetings and email communications. For the second year of PhD work, the experimental work is ongoing at KIT since November until December 2014.

On the other hand, an air oxidation research community has been formed by PSI, EDF, GRS, IRSN, KIT and IBRAE. The mentioned partners participate actively in seminars and workshops in order to share the state of the art of the air oxidation experimental studies and modelling.

Assessment 2014 and Perspectives for 2015

The work is progressing according to the plan. The following tasks were performed until the end of 2014.

Thermodynamic analysis: the work started with a review for relevant literature and data on oxidation in presence of nitrogen. The most influential processes in the nitride formation as well as the gaps in the data were identified during the literature review. The most influential process are the phase transformations during air oxidation in the Zr-O-N ternary system. Thus, conceptual mechanism of nitriding process is developed by integrating Zr-O-N literature, tests data and thermodynamic calculations within the first year of PhD study. The first publication was made based on the results of the first research task, thermodynamic analysis. The conference paper was prepared for the presentation at the NuMat 2014 conference (The Nuclear Materials Conference) in US on 27–30 October 2014. The title of paper is «A mechanism of nitriding process in the Zr-O-N system during air oxidation».

Separate effects tests: several sets of separate effect tests were performed at KIT during November to December 2014 to support the model development. The first series of experiments was aimed to identify the trigger condition for the nitride formation and the subsequent reoxidation of the nitrides. The second series was designed to confirm the mechanism of nitridation-reoxidation self-sustainability. In addition, Raman spectroscopy measurement is planned to investigate the phase compositions of the oxide scale in detail.

Model development: from the review of current air oxidation models, the weaknesses and limitations were identified. In addition, the main mechanisms which may play an important role in the model development were identified. The model development is ongoing in parallel with the experimental work.

A preliminary air oxidation model will be developed in 2015 and validated against independent data. Further publications and presentations are expected from the experimental work and the model development.

Publications

S. Park, The role of nitrogen during air oxidation, 19th International QUENCH Workshop, KIT, 19–21 November 2013

S. Park, L. Fernandez-Moguel, M. Steinbrück, J. Birchely, H.-M. Prasser, H.-J. Seifert, A mechanism of nitridation process in the Zr-O-N system during air oxidation, NuMat 2014: The Nuclear Materials Conferences, 27–30 October 2014, Florida, US

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