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Improving High-Temperature Measurements in Nuclear Reactors with Mo/Nb Thermocouples

J.-F. Villard · S. Fourrez · D. Fourmentel · A. Legrand

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Abstract Many irradiation experiments performed in research reactors are used to assess the effects of nuclear radiations on material or fuel sample properties, and are therefore a crucial stage in most qualification and innovation studies regarding nuclear technologies. However, monitoring these experiments requires accurate and reliable instrumentation. Among all measurement systems implemented in irradiation devices, temperature—and more particularly high-temperature (above 1000°C)—is a major parameter for future experiments related, for example, to the Generation IV International Forum (GIF) Program or the International Thermonuclear Experimental Reactor (ITER) Project. In this context, the French Commissariat à l'Energie Atomique (CEA) develops and qualifies innovative in-pile instrumentation for its irradiation experiments in current and future research reactors. Logically, a significant part of these research and development programs concerns the improvement of in-pile high-temperature measurements. This article describes the development and qualification of innovative high-temperature thermocouples specifically designed for in-pile applications. This key study has been achieved with technical contributions from the Thermocoax Company. This new kind of thermocouple is based on molybdenum and niobium thermoelements, which remain nearly unchanged by thermal neutron flux even under harsh nuclear environments, whereas typical high-temperature thermocouples such as Type C or Type S are altered by significant drifts caused by material transmutations under the same conditions. This improvement has a significant impact on the temperature measurement capabilities for future irradiation experiments. Details of the

J.-F. Villard (✉) · D. Fourmentel · A. Legrand
Commissariat à l'Energie Atomique, Saclay, DEN/DANS/DRSN/SIREN, Bat 527–PC 92,
91191 Gif-Sur-Yvette Cedex, France
e-mail: jean-francois.villard@cea.fr

S. Fourrez
Thermocoax SAS, BP 26, 61438 Flers, France

successive stages of this development are given, including the results of prototype qualification tests and the manufacturing process.

Keywords High temperatures · Molybdenum · Niobium · Nuclear reactors · Thermocouples

1 Introduction

1.1 Context of In-Pile Measurements

Nuclear research reactors are widely used around the world for various purposes, such as irradiation of material or fuel samples, operation of reactor prototypes, safety studies, assessment of neutronic parameters (such as neutron absorption cross sections or reaction rates), production of artificial radio-elements, etc. Many experiments performed in these facilities require in situ measurements to monitor and control the conducted tests. These needs are particularly critical in material testing reactors (MTRs), which are specifically dedicated to the assessment of nuclear radiation effects on material or fuel sample properties. Irradiations carried out in MTRs are crucial phases in most scientific programs regarding nuclear technologies, such as research for the enhancement or qualification of nuclear fuels for current or future power reactors, the assessment of reactor materials ageing for lifetime increase studies, and in-pile tests of innovative devices for advanced reactors or material investigations.

In France, the Commissariat à l'Energie Atomique (CEA) has operated since 1966 the OSIRIS MTR in Saclay, near Paris, and is also preparing the construction of the Jules Horowitz Reactor (JHR). This 100 MW new generation MTR will begin operation in 2014 in Cadarache, in the South of France.

In MTRs, experiments are conducted in irradiation devices, introduced inside or beside the core of the reactor, containing material or fuel samples. The quality of these experiments depends, in large part, on the measurements performed in the devices. Parameters measured in situ typically include the neutron flux, temperature, sample dimensions, fission gas release, etc. These in-pile measurements require high-quality sensors that must satisfy the following criteria:

(i) high reliability, because irradiated sensors cannot be replaced or repaired easily;
(ii) very high accuracy, to satisfy continuously increasing scientific requirements;
(iii) capability to operate in harsh nuclear environments (neutron flux and gamma radiation in MTRs can exceed, respectively, $4 \times 10^{18}\,\mathrm{n \cdot m^{-2} \cdot s^{-1}}$ and $1.5\,\mathrm{MGy \cdot s^{-1}}$);
(iv) capability to operate in pressurized water, liquid metals, or high-temperature gas;
(v) miniaturized body, to be implemented in small irradiation devices without altering the nominal thermal conditions of the samples.

To ensure the quality of its current and future MTR experimental programs, the CEA has recently strengthened its research and development activities regarding innovative in-pile instrumentation [1].

1.2 In-Pile Temperature Measurements

Temperature is a key parameter for most irradiation experiments conducted in MTRs. In-pile temperature measurements have been performed for decades with MIMS-type (mineral insulation and metallic sheath) thermocouples.

For temperatures below 1000°C, needs are quite well satisfied using Type K or Type N thermocouples (Ni–Cr/Ni–Al or Ni–Cr–Si/Ni–Si), generally with alumina (Al_2O_3) insulation and a 1 mm outer diameter stainless steel or Inconel sheath. These sensors have demonstrated excellent reliability and signal stability under irradiation, even for very high integrated neutron fluxes exceeding $10^{26}\,n \cdot m^{-2}$ (thermal neutrons).

Major difficulties are associated with high-temperature measurements for long-term irradiations. As Type K and Type N thermocouples fail frequently under irradiation above 1000°C (the commonly accepted limit for Type K is about 1080°C), in-pile temperature measurements in this range have typically employed Type C thermocouples (W-Re alloys). However, under the influence of thermal neutron flux, Type C thermoelements transmute very rapidly. The susceptibility of an element to transmutation can be characterized by its neutron absorption cross section (NACS); the decrease of this component under irradiation is faster the higher its NACS. Type C thermoelements (tungsten and rhenium) with NACS of 18 barns and 90 barns, respectively, are quickly transformed into (mainly) osmium [2]. This significant change in the composition of the thermocouple wires causes an irreversible modification of its thermoelectric response, and induces a drastic and unacceptable signal drift that can reach tens and even hundreds of degrees Celsius after some weeks of MTR irradiation [3]. Furthermore, Type S thermocouples (platinum–rhodium alloys), which might appear to be an alternative for in-pile measurements, are also affected by an even larger decalibration than that of Type C because of the very high NACS (145 barns) of rhodium. Therefore, existing high-temperature thermocouples are unsuitable for long-term irradiations.

Because many future MTR experiments related, for example, to the Generation IV program or ITER project require reliable and stable in-pile measurements at high temperatures (typically between 900 and 1500°C, with a required uncertainty of about 1%), the need for an adequate measurement system has become strategic. For this reason, the CEA started in 2003 a research program to develop and qualify new high-temperature in-pile sensors. Among various on-going developments on this subject, a new type of thermocouple is being studied to satisfy MTR requirements.

2 Sensor Development

2.1 Component Selection

2.1.1 Main Criteria

Materials for wires, insulator, and sheath have been selected taking into account theoretical considerations, experience, and specific tests achieved within this study. The key parameters taken into account for all materials are principally:

(i) Melting temperature and mechanical properties (particularly ductility and corrosion resistance) at high temperature;
(ii) Interactions among materials over the complete temperature range;
(iii) Cost and availability.

Additional criteria have been considered for each part of the thermocouple. The materials for the wires had to satisfy the following:

(i) Significant magnitude of the thermoelectric signal;
(ii) Low susceptibility to transmutation, that is, a low NACS;
(iii) Compatible thermal expansions between coupled materials, to avoid mechanical stress when heated, because of different elongations.

For the insulation material, the main parameter is the value of the insulation resistance over the whole temperature range, which must stay high enough to limit current leakage. Sheath materials have to exhibit good machinability, and must also be compatible at high temperature with materials that will be in contact with the sensor.

2.1.2 Initial Selection

As a first technical step, the wires, insulator, and sheath materials were selected based on results from previous studies [4,5] and CEA's experience with in-pile applications. Table 1 summarizes the considered materials. The properties of molybdenum and niobium fully justify interest in this development. With respective NACS of 2.5 and 1.1 barns, these materials will remain almost unchanged by transmutation even after a long period of use for in-pile applications.

In the first phase of these studies, only pure Mo and Nb have been considered, to promote long-term availability and minimize dependence on material suppliers.

2.1.3 High-Temperature Compatibility Tests

These tests were performed in the Thermocoax Laboratory in Flers (France), using a 2000 °C induction furnace dedicated to high-temperature processes and calibrations (see Fig. 1).

Several samples comprising wires, ceramic insulators, and sheaths were assembled in a graphite barrel and tested at 1600°C under Arcal 1 gas (argon/helium mixture) for 24 h. Table 1 summarizes the results of this test.

Consequently, the first thermocouple prototypes were defined and manufactured as follows: pure Mo and Nb wires, HfO_2 insulator, and Nb sheath.

2.2 Prototype Manufacturing

2.2.1 Fabrication Process and Controls

As the characteristics (geometry and purity) of the components have a significant impact on the behavior of this thermocouple, the selection and purchase of the raw materials were carefully managed. Pure niobium (99.9%) tube, 1.6 mm outer diameter,

Table 1 Summary of main criteria for wires and sheath materials selection

Material	Neutron absorption cross section[a] (barn)	Melting temperature[b] (°C)	Result of high-temperature compatibility test[c]	Observation
Wires				
Nb	**1.1**	**2472**	**N/A**	**Selected**
Mo	**2.5**	**2622**	–	**Selected**
Pt	10	1768	–	Expensive
W	18	3414	–	Difficult welding
Re	90	3186	–	Expensive, high NACS
Rh	145	1963	–	Expensive, very high NACS
Sheath				
Ti	N/A	1670	Important reaction (carburization + cracking)	
Nb	–	**2472**	**Light carburization**	**Selected**
Mo–Re 50%	–	>2500	Important reaction (carburization + cracking)	
Mo	–	2622	Significant reaction (carburization)	
Ta	–	**3007**	**Light carburization**	**Could be selected**
Re	–	3186	Light carburization	Expensive, difficult machining

[a] NACS of main isotopes for thermal neutrons at 2200 $m \cdot s^{-1}$, from literature values [6]
[b] See Ref. [7]
[c] Results of 24 h test at 1600°C under Arcal 1 gas (argon/helium mixture), performed on assemblies including Mo and Nb wires (0.2 mm diameter), HfO_2 insulation, and sheath of the considered material, in contact with graphite

was selected for the thermocouple outer sheath. Pure molybdenum (99.95%) and niobium (99.9%) wires were selected and drawn to 0.23 mm diameter by the Thermocoax Company. Hard-fired hafnium oxide (99.9%) insulators with single and double bores were chosen to be compatible with the outer tube and the wires. The typical process used to fabricate these thermocouples includes:

(i) cleaning the sheath outer tube by high-temperature heat treatment under inert gas,
(ii) cleaning the thermoelectric wires with solvents and a bake-out process,
(iii) baking the insulator beads,
(iv) welding a closure cap on the sheath outer tube,
(v) stringing insulator beads on the thermoelectric wires and laser welding the hot junction,
(vi) stringing a single-bore insulator over the hot junction,
(vii) introducing all parts into the sheath tube up to the closure cap,
(viii) vacuum backing and helium filling,

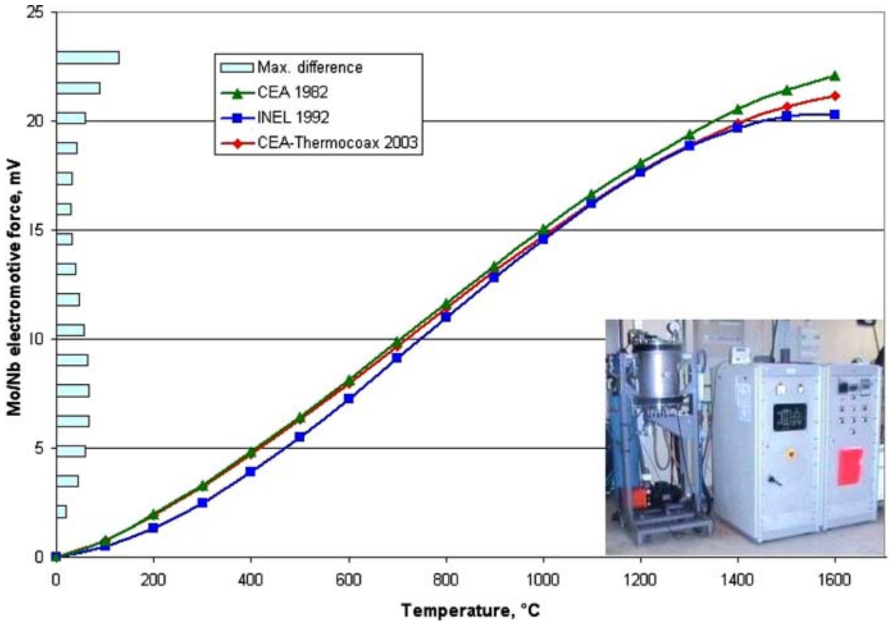

Fig. 1 Electromotive force of Mo/Nb thermocouples measured during calibration tests, compared with previous results obtained by CEA [8] and INEL [5]. The maximum difference between these three results is given as an indication of the electromotive force reproducibility. A picture of the 2000°C calibration furnace is also included

(xi) sealing the end tip with temporary resin, before assembling an extension cable,
(x) quality control by radiography (X-rays).

This work uses an industrial manufacturing process to produce the prototypes. The major benefits of this choice are the reproducibility of the fabrication method and the ability to ensure a long-term supply. Previous investigations reported, for example, in [8] and [5] were mainly based on tests conducted with bare wires installed in insulators. These early studies did not mention any comparable industrial manufacturing of small diameter (<2 mm), sheathed Mo/Nb thermocouples.

2.2.2 Thermal Stabilization

The thermoelectric signal of a thermocouple must be stable and repeatable over the whole temperature range. Calibration tests performed on Mo/Nb thermocouples up to 1600 °C demonstrated that these thermocouples are not stable and not repeatable without some initial thermal stabilization. Parasitic thermal drifts are principally attributed to migrations of chemical elements around the hot junction and to annealing of mechanical stresses induced during manufacturing by the mechanical operations. Therefore, adequate stabilization by heat treatment under inert gas was investigated, defined, and then applied to the Mo/Nb thermocouple prototypes.

The duration of the heat treatment should obviously be long enough to stabilize the signal. This parameter can be easily determined by monitoring the signal delivered by the thermocouple during the treatment. We determined that a 20 h high-temperature anneal is an appropriate compromise to stabilize the signal and to limit embrittlement of the sheath and wire materials due to the treatment. We also determined that the temperature of the heat treatment should be at least 150°C higher than the maximum operating temperature expected for the thermocouple. As an indication, Mo/Nb prototypes designed to be used at a maximum temperature of 1200°C have been preliminarily stabilized by 20 h at 1400°C.

2.3 Thermoelectric Characterization of Mo/Nb Pair

Using the same facility as for previous high-temperature compatibility tests, a complete calibration of the Mo/Nb thermocouple was achieved, to assess its thermoelectric response in the considered temperature range. The Mo/Nb thermocouple was calibrated against a Type S thermocouple.

Figure 1 shows the result of the Mo/Nb calibration from ambient to 1600°C. This sensor exhibits a reproducible response of about $14\,\mu V \cdot {}^{\circ}C^{-1}$ in the (1000–1600)°C range. This signal is of the same order of magnitude as those of standard high-temperature thermocouples, and is definitely compatible with input ranges of conventional data acquisition systems. One can also note that the Seebeck coefficient of the Mo/Nb thermocouple decreases with increasing temperature above 1000°C.

The calibration curve obtained during this study is consistent with results previously obtained at CEA [8] and INEL [5].

3 Testing

3.1 Out-of-Pile Endurance Test

3.1.1 Bench Tests and Protocol

A major phase in the qualification of the selected prototype is high-temperature endurance testing. The goal is to assess both the reliability and stability of the sensor when used under nominal conditions, except for nuclear radiations. As these new sensors are expected to be first used in the OSIRIS reactor for irradiation experiments related to high-temperature reactors (HTR) studies, we chose to perform qualification tests with conditions as close as possible to this particular application. For this reason, the first out-of-pile endurance tests of Mo/Nb thermocouples were conducted at 1100°C on a graphite support. Other kinds of commercially available thermocouples, including Types K, N, and C, were tested simultaneously in the same environment to assess the features that can have a significant impact on their performance, such as wire diameter or raw material suppliers. A specific bench test based on a high-temperature electric furnace was assembled and operated in the Thermocoax Laboratory. Thermocouples were exposed to a regulated temperature of 1100°C, in a low flow of inert gas, while positioned in contact with nuclear-grade graphite. This test ran for 2500 h, with intermediate visual examination after 500 h.

3.1.2 Results and Expected Improvements

Figure 2 exhibits the main results of this 2500 h operation. The best stability was obtained with Type N and Type K thermocouples, especially with large diameters (1.5 mm). However, this does not mean that they are suitable for higher temperatures, particularly for in-pile use. Above 1100°C, only Type C or Mo/Nb will remain usable for in-pile measurements. Moreover, if the out-of-pile behavior of Type C is recognized to be excellent (as measured during this test), one must remember that the expected drift of this sensor under irradiation will exclude their use for long-term in-core measurements. As an indication, Fig. 2 includes a representation of the expected in-pile drift of a Type C thermocouple when exposed to a thermal neutron flux of $4 \times 10^{18}\,\mathrm{n \cdot m^{-2} \cdot s^{-1}}$, which is typical of a MTR core environment (this calculation is based on literature values from in-pile measurements reported in [3] and [9]).

The Mo/Nb prototype failed after 1800 h, and at the beginning, its signal was affected by a negative drift of up to −50°C (i.e., 4.5%) during the first 250 h at high temperature, before increasing positively. Such a response demonstrates that different

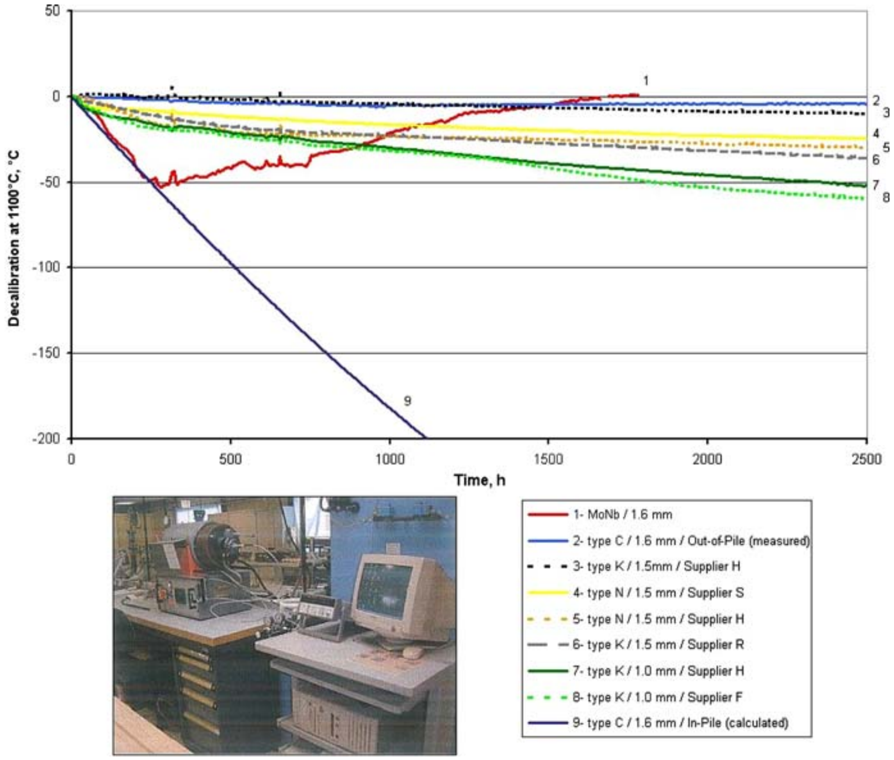

Fig. 2 Evolution of the signal measured by different thermocouples during the endurance test at 1100°C, and indication of the expected in-pile drift of a Type C thermocouple under a constant thermal neutron flux of $4 \times 10^{18}\,\mathrm{n \cdot m^{-2} \cdot s^{-1}}$ (this last calculation is based on literature values from in-pile measurements reported in [3] and [9]). A picture of the specific high-temperature bench test is presented under the graph

and successive phenomena occurred in this thermocouple during its operation. This prototype exhibited a very small residual drift of less than 2°C (i.e., <0.2%) at the end of its running time, but its behavior is obviously not fully satisfactory. We assume that the main causes of the observed phenomenon are:

– annealing of mechanical stress induced by wire preprocessing that was performed during sensor assembly to match the geometry of the insulator,
– materials oxidation and carburizing. Strong oxidation signs were observed on the thermocouple sheaths after opening the furnace. This indicates that interactions due to the unexpected penetration of oxygen occurred during the tests.

Some improvements are now being tested to increase the reliability and stability of Mo/Nb prototypes. A first enhancement consists of changing the geometry of the ceramic insulation, with the goal to reduce the mechanical premachining of the wires during sensor assembly. Further progress should come from the use of Mo and Nb alloys instead of pure metals. The advantages of alloys have been well recognized for standard thermoelements, both for reliability and for stability [8].

3.2 In-Pile Qualification

At the end of the development process, an in-pile qualification is required to validate sensor performances in nominal nuclear conditions. Therefore, a specific in-pile experiment has been prepared by CEA and will be irradiated in the OSIRIS reactor. The goal of this experiment is to measure the evolution of signals from different thermocouples (including Mo/Nb prototypes) during high-temperature irradiation, and to assess residual drifts as a function of the integrated neutron flux. The experiment developed for this purpose is based on a high-temperature fixed point [10]. This method has the advantage of delivering a reference point at the copper freezing temperature that can be compared with the corresponding measurements given by sensors. Due to the low NACS of copper (3.8 barns [6]), the effect of transmutation on the reference temperature will remain insignificant. As illustrated in Fig. 3, the thermocouples to be tested in the "Thermex" irradiation device will be positioned in a graphite tube containing pure copper heated by gamma radiation and additional electric heaters. The in-pile qualification of optimized high-temperature thermocouples is expected to be completed before 2010.

4 Conclusion

Innovative thermocouples designed to have a significant impact on the capability to operate long-term high-temperature measurements in nuclear reactors have been studied by CEA with technical contributions from the Thermocoax Company. Materials for wires, insulation, and sheath have been selected through high-temperature compatibility tests. An adequate manufacturing process and a thermal stabilization procedure have been defined. The thermoelectric response of the Mo/Nb thermoelements has been assessed, and out-of-pile endurance tests have been performed at 1100°C.

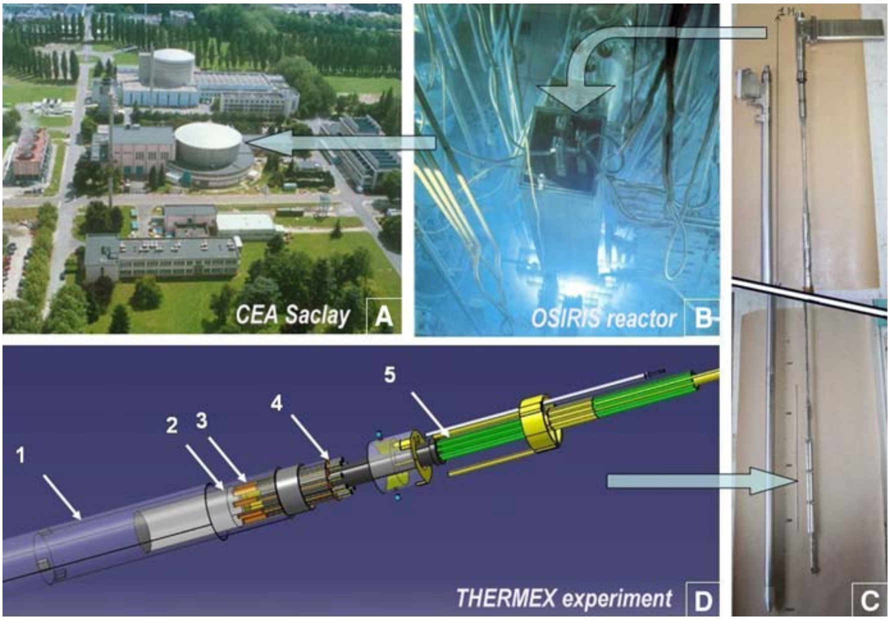

Fig. 3 Pictures of Thermex irradiation device: in the hot part of the experiment (**d**), high-temperature thermocouples (5) are inserted in a graphite barrel (2) filled with pure copper (3) and heated by gamma radiation and electric heaters (4); this assembly is placed in a stainless steel capsule (1 and **c**), which will be irradiated in the OSIRIS reactor core (**a** and **b**)

Improvements are still in progress to enhance the stability and reliability of the first prototypes tested, but the final in-pile qualification of this new Mo/Nb thermocouple has already been prepared for the French research reactor OSIRIS.

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