

The Centrifugal Liquid Wall Furnace

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Received 23 July 1968, and in revised form 11 December

The construction and operation of a centrifugal liquid wall furnace is described. A symmetrical molten cavity was formed within a hollow, thick-walled core of alumina, zirconia or magnesia by convective heating from an arc plasma jet. The core was rotated so that the liquid layer or layers formed from core material and from materials dispensed into the furnace were held centrifugally against the cavity wall.

The furnace was used to distil various oxides including alumina. In general, submicron-sized aerosols were obtained which require further investigation. X-ray diffraction showed that distilled alumina contained δ -alumina and probably γ -alumina. Distillation of impure alumina resulted in a near hundredfold increase in the proportion of gallium.

Examination of a fused alumina core usually revealed the growth of a crystalline tube from within the cavity against the plasma jet. This was at least partly due to crystal growth from the vapour-phase, but there was evidence of partial melting or remelting of the tube possibly by radiation from the arc column of the plasma jet.

1. Introduction

Recent interest in the manufacture of new materials with exceptional properties (e.g. whiskers), has underlined the difficulties of containing solids and liquids in chemically pure environments at elevated temperatures. At temperatures above 3000°C, there are few solid materials available from which crucibles can be made, particularly for the containment of liquids. In the liquid wall furnace described by Grosse, one liquid is made to float on a second underlying liquid layer, previously formed by melting the inside of a suitable tube [1]. The liquid layers are held in place centrifugally by rotating the tube rapidly about its major axis.

A furnace utilising a similar principle has been constructed and operated (fig. 1). The heat source was a plasma jet which directed a stream of very hot gas or plasma along the axis of a ceramic core. The design was adapted so that the furnace could be operated continuously, thus enabling various oxide materials to be distilled from the furnace in quantities of the order of 10 g/h.

2. Furnace Construction

Initial experiments were performed using sint-

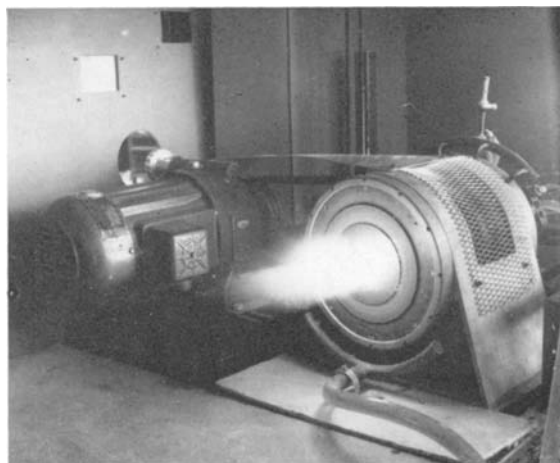


Figure 1 Furnace photograph.

ered alumina tubes of about 20 mm diameter and 2 mm wall thickness. Such tubes could be melted internally, but cracking usually occurred. Hence it was decided to try thick wall tubes or cores made from slip cast alumina, as these could be made quickly at small expense. Such cores have proved to be remarkably thermal shock-resistant

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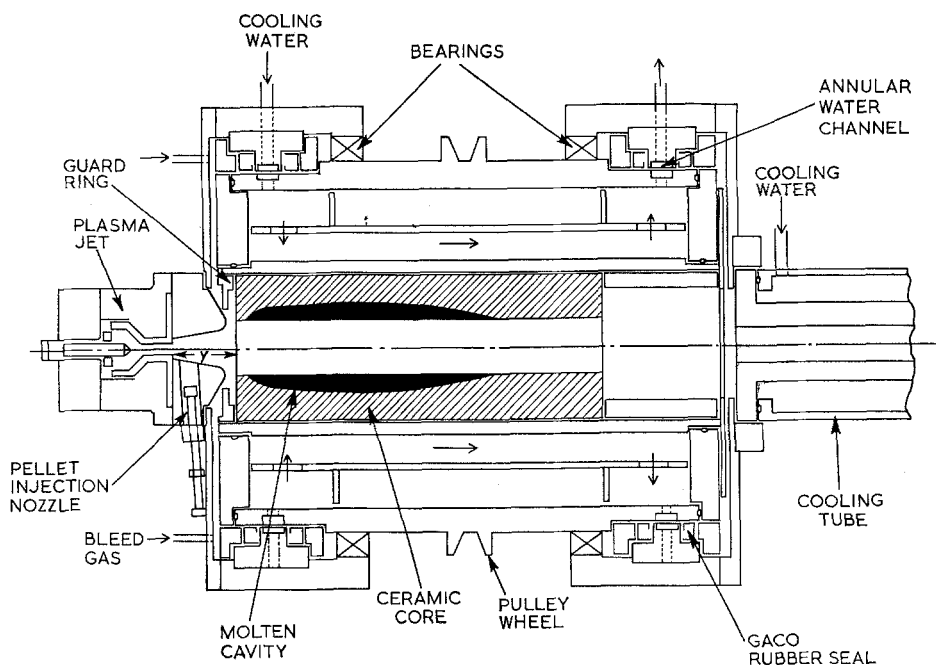


Figure 2 Drawing of furnace section.

and impervious, but instead of obtaining a regular sectioned tube of molten material [1], a cavity of roughly elliptical section was formed. Similar cores have been made from castable zirconia and magnesia by using an outer supporting tube of alumina (Super Refractories Ltd).

The ceramic core was supported by a water-cooled steel sleeve within the furnace, which was rotated axially at a speed of about 700 rpm by means of a variable speed motor unit (fig. 2). The arc plasma jet torch used has been described elsewhere [2].

Metal oxides to be melted within the furnace were usually introduced as pellets 1 cm in diameter made using a pellet press, but rods of compacted material were made by hydrostatic compression [3]. Initially, pellets were introduced manually into the furnace by means of a long stainless steel spoon but subsequently introduction was effected by means of an injection nozzle sandwiched between the plasma torch and the furnace (fig. 2). Gaseous products emerging from the furnace were cooled by passage through a cooled metal tube which was connected to a vertical electrostatic precipitator for the recovery of distilled materials.

3. Operation

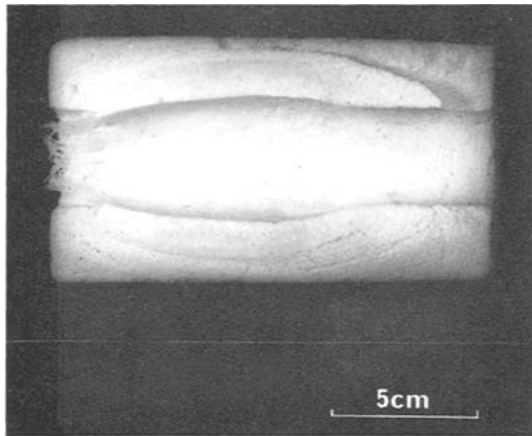
Cast alumina cores were melted successfully by the use of helium, helium-hydrogen, argon-

hydrogen or argon-nitrogen plasma jets. Melting was not achieved with argon alone even at maximum power conditions and helium could not be used to melt cores of internal diameter greater than about 18 mm. An elliptical cavity about 10 cm long was readily formed by using gas mixtures containing hydrogen (fig. 3a).

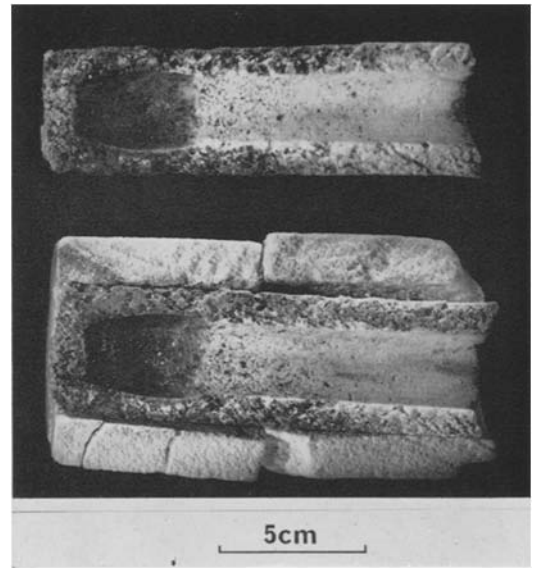
With practice it was possible to control the melting of the core, by altering slightly the composition of the plasma gas and so avoiding overheating which produced constrictions at the ends of the molten cavity. The exact position, shape and size of cavity formed depended on various factors (table I).

The melting of a zirconia core required a plasma jet of higher enthalpy than was necessary for the same size alumina core and the cavity formed was smaller (fig. 3b). An important feature was the relatively low volatility of zirconia which made it particularly useful as a furnace lining. Similar conditions were used for the melting of magnesia cores, but these were not so useful because of the comparative volatility of this material.

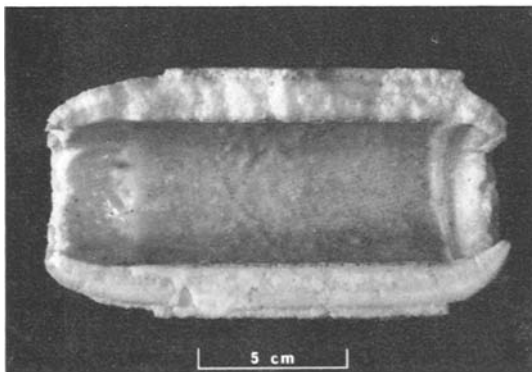
Observation of the inside of the furnace was only possible when it was discharging directly to the atmosphere. The difficulty of observing the inside of the narrow cylindrical core was increased by the formation of a molten cavity and by the presence of intense radiation from the



(a)



(b)



(c)

Figure 3 Cavity sections - a, b and c.

plasma jet. Visual observation was carried out through suitable filters placed between the observer and a plane viewing mirror on the furnace axis. Some observations along the axis were made through a small aperture in an asbestos screen with a rotating sector stroboscope in order to examine cavity symmetry and with an optical pyrometer (Leeds and Northrup) to measure furnace wall temperature.

The stroboscope observations indicated that when the speed of rotation was less than about 500 rpm, the cavity tended to become unsymmetrical. A core speed of 500 rpm was equivalent to a wall acceleration of about 6 g, which was

well above the critical speed for the stable "rimming" of a liquid within a rotating tube [4]. Temperature measurements indicated variations of several hundred degrees within a molten alumina cavity and maximum temperatures approaching 3000° K have been obtained within a zirconia core.

4. Examination of Cores

Typical cavity sections cut by a diamond impregnated wheel are shown in fig. 3. When the inside of an alumina core was melted for the first time, the liquid alumina formed was driven by centrifugal force into the underlying porous material. After penetrating some distance, the liquid resolidified to give a strong impenetrable shell. Cavity sections showed several layers: an inner, completely fused layer which formed the liquid wall of the furnace, a second fused layer containing gas bubbles and sometimes well defined outward growing crystals and a third impervious layer formed by the complete penetration of porous material by the mobile liquid alumina. This outer layer was remarkably strong, both mechanically and in its ability to withstand thermal shock.

The innermost fused layer obtained by the use of a nitrogen-containing plasma jet was dark in colour (fig. 3c). Chemical analysis indicated that this was due to the presence of electrode materials (0.01% tungsten after a melting experiment lasting 45 min) and was not associated with any

significant change in the nitrogen content of the core material.

The most interesting feature observed was the growth of a constricting crystalline alumina tube during the initial melting of an alumina core (fig. 3a). This appeared to be due to the joining together of numerous crystals whose direction of growth was principally against that of the plasma jet, but which also grew sideways at a slower rate. Crystal growth occurred irregularly at a series of points and led to the formation of small whiskers of alumina.

When examined microscopically at $\times 250$ these whiskers did not show any grain-boundaries that could be detected by the use of polarising filters and it seems likely that they were single crystals. The large parent crystals, however, showed some grain-boundaries and surface imperfections which suggest that partial remelting of the crystal had taken place. X-ray powder diffraction of this crystalline material showed the presence of α -alumina.



Figure 4 Alumina whiskers stereoscan (gulleys).

The surface details of a typical crystal fragment about 1 cm long were observed by coating the fragment with a palladium-gold layer 500 Å thick and examining it by means of a Stereoscan Electron Microscope. Observation at a magnification of $\times 20$ revealed a system of shallow rounded gulleys covering the surface of the fragment (fig. 4). Examination of the whisker tips at high magnification ($\times 4000$) showed a comparatively rough surface with occasional spike-

like features that could be crystal growth sites (fig. 5).



Figure 5 Alumina whisker growth site.

5. Vaporising Experiments

During the formation of a molten cavity within a cylindrical alumina core some of the core material volatilised and was collected, but once a stable cavity was formed (after about 30 min) very little subsequent volatilisation occurred. Pure alumina rods could then be attached inside the cold cavity prior to reheating, or alternatively alumina pellets were dispensed directly into the molten core.

In this way samples of volatilised alumina of commercial purity (core material) and of high purity were obtained. Distillation experiments were performed both under neutral conditions (helium only) and under reducing conditions (argon + hydrogen). By a similar method zinc oxide, sodium chloride, magnesia, ceric oxide and manganous oxide were distilled from alumina cores and magnesia and ceric oxide were distilled from zirconia cores.

6. Examination of Vaporised Oxides

The complex nature of these materials requires lengthy investigation and so the work that follows must be regarded as a preliminary examination. Materials condensed in the cooling tube were usually contaminated with core material blown out of the furnace, but materials recovered from the precipitator were very fine powders that readily formed aerosols in a stream of gas. These aerosols were examined. The condensed alumina

Plasma jet			Bleed gas		Core material	Internal dia. mm	Cavity (approximate dimensions)		Photograph fig. 3
Gas composition % (by volume)	Flow 1/min	Approximate heat input kcal/min	Flow 1/min	Flow 1/min			Max dia. mm	Length mm	
He 100	90	202	—	—	Al ₂ O ₃	18	34	150	
He 97 H ₂ 3	93	229	—	—		18	36	140	
Ar 73 N ₂ 27	74	349	N ₂	5		33	46	140	c
Ar 98 H ₂ 2	55	176	H ₂	8		33	48	100	
Ar 95 H ₂ 5	85	232	Ar	10		27	34	80	
Ar 93 H ₂ 7	58	216	Ar	7		33	47	100	a
Ar 90 H ₂ 10	60	232	Ar	8		33	45	140	
Ar 85 H ₂ 15	64	266	H ₂	8		33			
Ar 93 H ₂ 7	60	229	Ar	7	ZrO ₂	27	32	50	b
Ar 90 H ₂ 10	60	232	H ₂	8		27			
Ar 85 H ₂ 15	64	246	H ₂	8		27			
Ar 90 H ₂ 10	60	230	H ₂	8	MgO	27	30	60	

was a grey or greyish-blue powder in which particles down to 0.2 μm diameter were identified. These were grouped in aggregates of up to about 100 μm across. Examination by means of a JEM 7 Electron Microscope showed that these particles were filamentary in structure and seemed to consist of fused masses of the order of 300 \AA diameter joined by thin filaments (fig. 6). Two surface area measurements gave results close to 70 m^2/g .

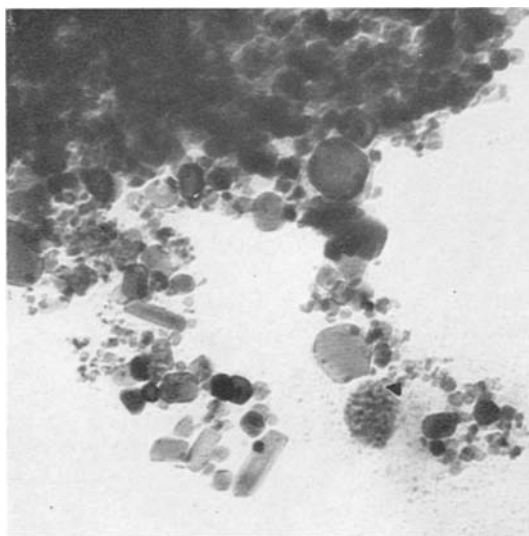


Figure 6 Vaporised alumina. Electro micro ($\times 148\text{k}$).

X-ray diffraction data of this material was not easy to interpret. Lines due to α -alumina were

definitely identified in some samples but were absent in others. From their appearance these lines could have been due to coarse core material blown out of the furnace. The remaining lines were conspicuous and were reproduced in many samples. Some of these have been definitely identified as being due to the presence of δ -alumina and others probably to γ -alumina. This still leaves many lines unidentified and it is possible that a novel alumina structure may have been produced which could be of interest as a catalyst material.

An analysis of volatilised alumina of commercial purity obtained from a core melted for the first time, showed that significant changes took place in the proportions of certain inorganic impurities on distillation. In particular the proportion of gallium increased nearly a hundredfold from 0.007 to 0.5%. Chemical tests were also made on the pure vaporised alumina to determine whether partial reduction occurred on vaporisation in the presence of hydrogen [5]. As it was not possible to exclude the atmosphere during the recovery of samples from the precipitator, these results must be treated with reserve. They showed that the proportion of reduced material was equivalent to only 0.5% of aluminium metal in the vaporised product. Furthermore, there was no apparent difference between alumina vaporised under reducing conditions (in the presence of hydrogen) and alumina vaporised under neutral conditions (helium only).

Magnesium oxide was distilled by various methods in a reducing atmosphere, but no change in composition was detected. Electron

Approximate heat balance %

To plasma jet	To pellet nozzle	To furnace coolant	To cooling tubes or effluent	Balance
45	—	27	7	21
30	—	17.5	—	52.5
32	—	25	7	36
33	21.0	22	—	24
28	—	13	—	59
38	—	35	15	12
36	—	26	12	26
31	19.0	22	7	21
31.5	19.0	23	16	10.5
33.5	20.5	23	14.5	8.5
36	16.5	15.5	—	32

micrographs showed it to be similar in particle size and structure to vaporised alumina (fig. 7) and surface area measurements gave very similar results. As a means of producing powders of large surface area, distillation seems to be inferior to other available methods, although it is several times more effective than grinding for powders in this size range (about $1 \mu\text{m}$). Ceric oxide was distilled from a zirconia core in the presence of hydrogen. The products showed a well-defined crystalline structure with separate particles of about 250 \AA minimum size (fig. 8).

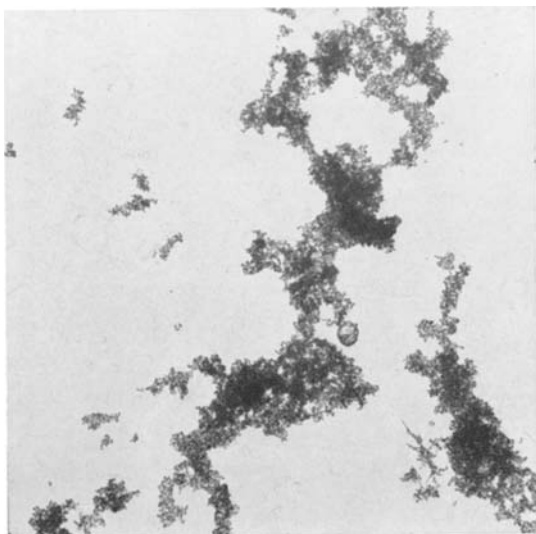


Figure 7 Vaporised magnesia. Electro micro ($\times 8k$).

7. Discussion

The ceramic core was heated convectively by

TABLE I The melting of ceramic oxide cores: optimum conditions and thermal measurements

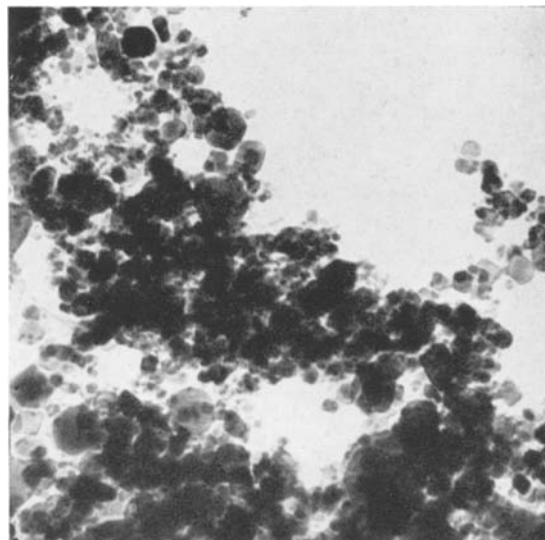


Figure 8 Vaporised ceric oxide. Electro micro ($\times 165k$).

contact with the plasma jet and heat balance measurements showed that under favourable circumstances using alumina cores, about half the electrical energy supplied to the plasma jet appeared as heat in the ceramic core (table I). At equilibrium, this heat flux was approximately equally divided between two dissipating processes: radial conduction through the porous core body to the water-cooled steel furnace tube and radiation from the molten interior out of the ends of the furnace.

Examination of core sections showed that the central regions of the molten cavity where the supporting core was thinnest were the hottest parts. It would seem that in spite of a larger conductive heat loss to the furnace coolant, as compared with the other parts of the cavity, the central regions were hotter probably because they could not radiate directly out of the ends of the furnace.

Convective heat transfer between the plasma jet and core was improved by the presence of a small proportion of a diatomic gas (hydrogen or nitrogen). Nitrogen mixtures were less convenient to use because of contamination of the core but the cavities produced were remarkably large and symmetrical (fig. 3c). An important feature in the use of hydrogen-containing mixtures was that it was possible to avoid overheating by reducing slightly the proportion of admixed hydrogen.

In order to obtain stable containment of a molten pipe of material within a rotating core melted on the inside, the density of the contained liquid must be less than that of the molten core material. Using an alumina core this limits the material density to 3 g/cm^3 at the melting point of alumina [6]. Molten zirconia is denser but precise values are not available because stabilising agents are present. Thoria seems to be an ideal material and Grosse and co-workers claim to have melted thoria tubes [7], but fabrication presents difficulties. It is desirable that the core material should be a poor conductor of heat and that it should be liquid over a large temperature range. Although manganous oxide and magnesia have high boiling points both are readily volatile at lower temperatures.

If a metallic oxide is melted within an alumina core, then in general it will be at least partly miscible with the molten alumina. With manganous oxide and alumina, the phase diagram indicates the formation of a eutectic mixture with a melting point of 1790° K [8]. Alumina also readily forms anionic and cationic complexes in the molten phase. Complications arising from the interaction of oxides could significantly be reduced by using another core material. Cahill and Grosse have reported the melting of zirconium carbide and niobium carbide within a rotating graphite tube heated internally by means of an arc [9]. A similar device using a molten cavity instead of a tube has recently been reported [10].

An interesting feature observed during the melting of an alumina core was the growth of a constricting crystalline tube out of the core against the direction of gas flow. This did not occur with zirconia or magnesia, which might have been because molten zirconia is more viscous than molten alumina and that magnesia is more volatile than either. Crystalline growth from the liquid-phase does not at first seem likely, because the required direction of liquid flow from inside the cavity would be opposed by the plasma jet.

Crystal growth from the vapour-phase seems more likely because vaporised material is known to be present in the furnace effluent. Initially, small seed crystals formed from the liquid-phase could grow by contact with vapour brought from the core interior by a turbulent retrograde gas stream moving along the core wall. The existence of such a flow has been demonstrated by the deposition of vaporised material on the face of

the plasma jet nozzle. This retrograde gas stream was opposed by the bleed gas (fig. 2) and it has been observed that crystal growth was reduced by increasing the bleed gas flow. The core region where crystal growth took place was close to the arc column of the plasma jet and it is possible that radiation from the arc column played a part in promoting local heating.

Examination of the crystals formed gave contradictory evidence as to the mechanism of their formation. The long outward growing crystals were usually rounded and were at least partly melted or remelted. In addition their surfaces seemed to be largely covered by a transverse system of rounded gulleys which is characteristic of crystals grown out of a liquid-phase; however, attached to the sides of these were smaller crystals of more clearly defined habit, which took the form of whiskers and seemed to be single crystals. There does not seem to be any doubt that these grew from the vapour-phase. The growth of alumina whiskers entirely by vaporisation in a hydrogen gas stream has been described by Sears and De Vries [11] and the growth of thoria crystals using a solar furnace by Laszlo *et al* [12].

A likely explanation for the crystal growth observed is that condensation from the vapour state was followed by slow remelting of the crystal structure, possibly by radiation from the arc column of the plasma jet. It is possible, however, that crystal growth from both the liquid and vapour states took place simultaneously, the former predominating in the early stages.

Acknowledgement

The authors are indebted to Dr D. A. Everest, who suggested the problem, for his interest and advice. They also gratefully acknowledge help from Dr J. A. Champion, and from the staff of NPL. The authors would also like to thank Mr Desty and Mr Allum of BP Research Ltd for surface area measurements and some interpretations of X-ray diffraction data.

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