The advantages of rammed unfired linings are well known: firing of the refractories is dispensed with, intricately shaped linings can be produced in monolithic form, and the work involved can be mechanized.

The spalling resistance of rammed linings is higher than that of linings of fired products [1, 2].

The literature contains only scant information about ramming compounds based on zirconium dioxide. Usually only the composition of the binders suitable for these compounds is described but even this limited data is frequently contradictory.

For example, some workers* [3-5] recommend phosphate binders for zirconia compounds while others [6-10] show that P₂O₅ inclusions are impermissible because even a small proportion interacts with the CaO and causes destabilization of the solid solution of zirconia.


Fig. 1. Variation ΔV/V of the volume, of the porosity P, of the apparent density γ, and of the cold-crushing strength σscr of zirconia ramming compounds with the heating temperature and the proportion of H₃PO₄. The first figure against the curves indicates the maximum grain size, the second figure the proportion (vol. %) of H₃PO₄.

TABLE 1. Variation of the $P_2O_5$ Content in Heated ZrO$_2$ Specimens

<table>
<thead>
<tr>
<th>Added $H_3PO_4$, % in terms of $P_2O_5$</th>
<th>$P_2O_5$, % after firing at a temperature ($^\circ$C) of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>150</td>
</tr>
<tr>
<td>5</td>
<td>5.04</td>
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<tr>
<td>3</td>
<td>3.04</td>
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</table>

It was found [11,12], however, that in spite of the destabilization of the solid solutions phosphate binders can be used for zirconia-based mortars. A mortar of this type has been tested and is now used in the lining of high-temperature furnaces constructed of zirconia refractory bricks.

Later [4] it was stated that in spite of the destabilization of the cubic solid solution in the system ZrO$_2$ -CaO phosphate binders can be used for zirconia batches at temperatures above 1600$^\circ$C. The grain size of the batches investigated was finer than 0.2 mm and the batches can be used for mortars and various coatings.

In this article the results are reported of development work on the composition of low-shrinkage ramming compounds for the lining of high-temperature furnaces.

The composition of the commercial zirconia used was as follows: 97.6-98.2% ZrO$_2$ + HfO$_2$, 0.64-0.80% TiO$_2$, 0.3% SiO$_2$, 0.02% Al$_2$O$_3$, 0.06-0.08% Fe$_2$O$_3$, 0.6-0.3% CaO, 0.10-0.12% MgO.

The zirconia was stabilized with 6 wt. % calcium oxide at 1750$^\circ$C as described elsewhere [13], ground, and screened to fractions of 5-2, 2-0.5 and finer than 0.5 mm. Some of the material was fine-ground to grain sizes finer than 0.088 and finer than 0.003 mm. The powders were either magnetically centrifuged or washed clean of iron with concentrated HCl.

A monoclinic zirconia, moreover, was fine-ground in a vibro mill.

The chemical composition of the stabilized zirconia was as follows: 93.28% ZrO$_2$ + HfO$_2$, 0.30% SiO$_2$, 0.02% Al$_2$O$_3$, 0.60% TiO$_2$, 0.08% Fe$_2$O$_3$, 5.60% CaO, 0.12% MgO.

The binder was orthophosphoric acid of density 1.72 g/cm$^3$ and was added to the body in proportions of 3 and 5 vol. % (approximately 3 and 5 wt. % in terms of $P_2O_5$).

The ramming compounds were produced from powders with two different grain size distributions (maximum grain sizes 2 and 5 mm). The fraction finer than 0.09 mm did not exceed 40%.

A proportion of monoclinic unfired ZrO$_2$ was added to the body to promote the formation of the phosphate bond [12].

The properties of the bodies in relation to the firing temperature are shown in Fig. 1. Up to 1000$^\circ$C no volumetric changes occur. At 1000-1400$^\circ$C the body opens, porosity increases, and the apparent density and strength decrease.

The strength of the body remains high enough (over 100 kg/cm$^2$), however, to give a lining of design strength.

No significant differences were noted to arise between the properties of batches with dissimilar grain size distributions with the addition of 5 vol. % $H_3PO_4$ although the porosity was slightly higher and the strength lower in the case of the batch with 2 mm grains.

Shrinkage was greater in the batches with a maximum grain size of 2 mm than in those with a maximum grain size of 5 mm so that coarse-grain powders would be preferred for unfired linings.

The porosity of the specimens increased over the whole temperature range when the proportion of orthophosphoric acid in the body was reduced from 5 to 3 vol. %. Compacting conditions improve, therefore, with an increase in the proportion of orthophosphoric acid.

![Fig. 2. The shrinkage of the concrete as a function of the proportion of added orthophosphoric acid and water after firing at 1750$^\circ$C. The figure against the curves indicates the proportion of liquid phase in the body.](image-url)