# BADDELEYITIC-CORUNDUM RAMMING REFRACTORIES MADE FROM WASTE RAW MATERIALS

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The possibility of utilizing baddeleyiticcorundum waste material for the production of high-grade ramming refractories exhibiting satisfatory strength has been proved experimentally. The refractories were bonded chemically with aluminium hydroxychloride.

#### INTRODUCTION

The present paper is based on the results of diploma theses worked out at the Institute of Glass and Ceramics and dealing with the utilization of materials obtained during reconstructions of glass melting furnaces lined with baddeleyitic-corundum blocks. The crushed material obtained can be advantageously utilized as a secondary raw material for baddeleyite-corundum refractories showing excellent chemical durability and resistance to thermal shock.

## **EXPERIMENTAL**

#### Raw materials

The baddeleyite-corundum crushed material should be carefully sorted because of some aspects which may seriously affect the quality of the final product. In the first place, the crushed material should contain the largest possible proportion of crystalline phase and the minimum amount of glassy phase. In the manufacture of cast baddeleyitecorundum blocks, the glassy phase is mostly concentrated at their centres as a result of the gradual cooling down, so that the surface layers should be preferred, also in manual sorting. One should also take into account that in the course of crushing, the glassy phase enters mostly the fine fractions, so that the coarse fractions should be used and only subsequently crushed to obtain the grain size distribution required.

# Bonding

The baddeleyite-corundum crushed material, which serves primarily as grog in the ramming refractories, should be selected from raw materials with  $Al_2O_3$  and  $ZrO_2$  contents at a ratio which simulates the content of the two oxides in the grog. Zirconia is provided in the form of zircon or zircon powder, alumina in the form of corundum or technical grade aluminium oxide.

To establish the optimum time of grinding of the bond, a test for the grinding limit was carried out, i.e. determination of the largest specific surface area of the bond in terms of the time of grinding. With the use of the customary 2% of antiagglomerating additives, the optimum time of grinding was found to be 80 minutes in a vibration mill for attaining a specific surface area of  $10.1 \text{ m}^2/\text{g}$  (the M 10 mill with a charging degree of 0.8, i.e. 40 kg of steel balls 7 to 15 mm in diameter and 3 kg of the material being ground).

#### Preparation of specimens

The compositions of the experimental mixes are listed in Table I. In the formulations, the grog was used in two grain sizes (designated BK 250/63 and BK 50/16, where the numbers signify the smallest and the largest particle size in  $\mu$ m), and the bond was added either ground or unground. The actual bonding agent (aluminium hydroxychloride), water and a small amount of dextrin (up to 1%) were introduced into a claw mixer and homogenized for 30 minutes. The mix was pressed into the form of cylinders 50mm in height and diameter, and prisms  $12\times+2\times120$ mm (under a pressure of 42.4 MPa). The specimens were dried for 24 hours at 130°C and fired in a bogie hearth furnace of the Karborundum Benátky works, at temperatures of 1410 and 1500°C respectively.

#### RESULTS

The basic criteria of success were density (bulk weight OH, water absorptivity by wt. NH, apparent porosity PZ, apparent density ZH), bending and compressive strength. The data obtained are summarized in Tables II and III.

From the standpoint of maximum bulk weight, formulation I.B appears as the best one, while the maximum strength was exhibited by formulation I.A. Both maximum values were achieved by firing at  $1500^{\circ}$  C. Equally suitable are formulations III.A and III.B. Generally speaking, the bulk weight after firing increases compared to the green one. With most of the specimens, the bulk weight after firing at  $1500^{\circ}$ C is higher than that after firing at  $1410^{\circ}$ C. The compressive strength depends on firing temperature more significantly than bulk weight, being higher at the firing temperature of  $1500^{\circ}$ C.

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| Table | Ι |
|-------|---|
|-------|---|

Composition of the experimental mixtures

| Designation                              | Grog                             |                                  | Bond                             |                                  | Binding agent<br>per dry mix    |  |
|--|----------------------------------|----------------------------------|----------------------------------|----------------------------------|---------------------------------|--|
|  | BK 250/63<br>[wt. %]             | BK 50/16<br>[wt. %]              | ground<br>[wt. %]                | unground<br>[wt. %]              | [wt. %]                         |  |
| I.A<br>I.B<br>I.C<br>I.D<br>II.A<br>II.B | 45<br>45<br>45<br>45<br>40<br>40 | 30<br>30<br>30<br>30<br>35<br>35 | 10<br>10<br>10<br>10<br>10<br>10 | 15<br>15<br>15<br>15<br>15<br>15 | 8<br>7<br>6<br>5 + HO<br>8<br>6 |  |
| II.C                                     | 40                               | 35                               | 10                               | 15                               | 5                               |  |
| II.D<br>III.A<br>III.B                   | 40<br>4O<br>40                   | 35<br>25<br>25                   | 10<br>20<br>20                   | 15<br>15<br>15                   | 4 + HO<br>7<br>6 + HO           |  |

Density criteria of the mixtures

| Designation  | Firing at 1410°C   |  |  | Firing at 1500°C   |  |   |  |  |
|--|--|--|--|--|--|---|--|--|
|  | OH<br>[kg/m³]  | NH<br>[%]  | PZ<br>[%]  | ZH<br>[kg/m <sup>3</sup> ]   | OH<br>[ķg/m³]  | NH<br>[%]   | PZ<br>[%]  | ZH<br>[kg/m <sup>3</sup> ]   |
| I.A<br>I.B<br>I.C<br>I.D<br>II.A<br>II.B<br>II.C<br>III.D<br>III.A<br>III.A<br>III.B | 3148<br>3154<br>3106<br>3043<br>3156<br>3094<br>3016<br>3096<br>2914<br>2880 | 6.74<br>6.52<br>6.01<br>6.98<br>5.64<br>6.81<br>7113<br>6.72<br>8.68<br>8.62 | 21.2<br>20.6<br>19.2<br>21.2<br>17.8<br>21.1<br>21.5<br>20.8<br>25.3<br>24.8 | 3982<br>3895<br>3983<br>3994<br>3745<br>3822<br>3735<br>3820<br>3865<br>3816 | 3252<br>3317<br>3134<br>3037<br>3172<br>3029<br>3055<br>3125<br>2849<br>3021 | 4.77<br>3.39<br>6.O3<br>6.79<br>5,24<br>6.55<br>7.19<br>5.93<br>9.00 <sup>f</sup><br>6.73 | 15.4<br>11.3<br>18.7<br>21.2<br>16.6<br>19.8<br>21.7<br>18.6<br>25.6<br>20.3 | 3857<br>3816<br>3858<br>3861<br>3761<br>3787<br>3793<br>3843<br>3833<br>3764 |

#### CONCLUSION

The best properties were achieved with the material containing 45 wt. % of baddeleyite-corundum crushed material BK 250/63, 30 wt. % of baddeleyitecorundum crushed material BK 50/16, 10 wt. % of ground bond and 15 wt. % unground bond, with an addition of 7% or 8% of aluminium hydroxychloride as bonding agent (the latter addition is related to dry mix).

#### References

- Pešek J.: Candidate's Thesis at KTS VŠCHT Prague, 1984.
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- [3] Varmužová R.: Diploma Thesis at KTS VŠCHT Prague, 1989.

| Compressive strength opd, bending strength opo |                       |                       |                       |                       |  |  |
|--|-----------------------|-----------------------|-----------------------|-----------------------|--|--|
| Designation                                    | Firing at             | t 1410°C              | Firing at 1500°C      |                       |  |  |
|  | σ <sub>Pd</sub> [MPa] | σ <sub>Po</sub> [MPa] | σ <sub>Pd</sub> [MPa] | σ <sub>Po</sub> [MPa] |  |  |
| I.A  | 95.83                 | 24.00                 | 281.67                | 39.54                 |  |  |
| I.B  | 78.77                 | 24.00                 | 242.26                | 30.35                 |  |  |
| I.C  | 66.26                 | 24.42                 | 103.98                | 31.04                 |  |  |
| I.D  | 41.76                 | 18.84                 | 72.52                 | 24.62                 |  |  |
| I.D<br>II.A                                    | 42.27                 | 18.57                 | 49.30                 | 24.02                 |  |  |
| II.A<br>II.B                                   | 44.93                 | 25.77                 | 49.30<br>54.96        | 29.13                 |  |  |
|  |                       |                       |                       |                       |  |  |
| II.C   | 41.44                 | 23.97                 | 61.10                 | 29.12                 |  |  |
| II.D   | 31.71                 | 17.88                 | 42.72                 | 23.29                 |  |  |
| III.A  | 46.30                 | 4.52                  | 50.34                 | 12.75                 |  |  |
| III.B  | 21.69                 | 11.48                 | 31.79                 | 23.35                 |  |  |
|  |                       |                       |                       |                       |  |  |

Table III Compressive strength  $\sigma_{Pd}$ , bending strength  $\sigma_{Po}$ 

# BADDELEYITOKORUNDOVÉ DUSACÍ HMOTY Z DRUHOTNÝCH SUROVIN

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Materiál, vzniklý drcením baddeleyitokorundových odlévaných kamenů, které dosloužily ve sklářských tavicích pecích, lze použít jako surovinu pro dusací hmoty, které najdou své využití zejména při opravách vysokoteplotních agregátů opět ve sklářství. Bylo zjištěno, že nejlepších parametrů dosahuje hmota, tvořená 45% hm baddeleyitokorundové drtě BK 250/63, 30% hm baddeleyitokorundové drtě BK 50/16, 10% hm mleté vazby a 15% hm nemleté vazby. Vazba je tvořena kompozicí zirkonové a korundové suroviny tak, aby poměr základních oxidů byl takový jako ve zpracovávané baddeleyitokorundové drti. Jako pojiva je použito vodného roztoku hydroxidchloridu hlinitého v množství 7, resp. 8% hm.