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Which factors influence the bulk density and open porosity testing results for dense shaped refractory materials?

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Abstract

This paper highlights the efforts that were undertaken within the framework of the EU FP7 "ReStaR" research project for the determination of testing parameters and conditions (factors) influencing the bulk density (BD) and open porosity (oPo) testing results of dense shaped refractory materials. Besides the generation of precision data, it is necessary to understand which instructions in the standard EN 993-1 for dense shaped refractories are sensitive for diverging testing results and are therefore to be considered as significant factors influencing those results. Screening factorial designs were used to identify those significant factors in bulk density and open porosity testing of dense shaped refractories. For this material, up to fifteen possible factors were identified and set to two different levels each. Accordingly, 16-trial runs, taking into account the possible factors, were carried out in laboratories with this type of refractory. The analysis of variance method was used to analyse the testing results. For dense shaped refractories, results showed that the place of extraction of the samples (internal or external part of the brick) and the immersion liquid (water/paraffin) are factors that significantly affect the results of BD and oPo testing. On the other hand, the sponging material, the time of evacuation and the soaking time under water at ambient conditions were found not to influence the results of BD and oPo testing. A second design of experiment, which contained the four most significant factors, was studied for this refractory material in four different laboratories. Hereby estimations of the repeatability and of the reproducibility of the testing standards for BD and oPo across different laboratories were obtained. For the EN 993-1 standard tested on an alumina dense shaped refractory (not reacting with water as immersion liquid), a reproducibility of 0.07 g/cm^3 and a repeatability of 0.04 g/cm^3 were obtained for the BD and a reproducibility of 1.6 vol% and a repeatability of 1.2 vol% were obtained for the oPo.

Keywords: Bulk density, Open porosity, Testing, Shaped refractory materials, Reproducibility

JAKIE CZYNNIKI WPŁYWAJĄ NA WYNIKI BADAŃ GĘSTOŚCI POZORNEJ I POROWATOŚCI OTWARTEJ GĘSTYCH, FOMOWANYCH MATERIAŁÓW OGNIOTRWAŁYCH?

W artykule zwraca się szczególną uwagę na wysiłki podjęte w ramach struktury projektu badawczego EU FP7 "ReStaR" realizowanego w celu określenia parametrów oznaczania i warunków (czynników) wpływających na wyniki oznaczania gęstości pozornej (BD) i porowatości otwartej (oPo) gęstych, formowanych materiałów ogniotrwałych. Oprócz wygenerowania precyzyjnych danych, konieczne jest zrozumienie, które instrukcje w normie EN-993-1 dla gęstych, formowanych materiałów ogniotrwałych wrażliwe są na wywoływanie rozpraszania wyników badania i dlatego należy je uważać za ważne czynniki wpływające na te wyniki. Eliminujące eksperymenty czynnikowe użyto, aby zidentyfikować te czynniki w badaniach gęstości pozornej i porowatości otwartej gęstych, materiałów ogniotrwałych. W przypadku tych materiałów, zidentyfikowano aż piętnaście możliwych czynników i dla każdego wybrano dwa różne poziomy. Adekwatnie, biorąc pod uwagę możliwe czynniki, przeprowadzono serie złożone z 16 prób w laboratoriach na tym typie materiału ogniotrwałego. Metodę analizy wariancyjnej użyto do analizy wyników badań. W przypadku gęstych, formowanych materiałów ogniotrwałych wyniki pokazały, że miejsce pobierania próbek (wewnętrzna lub zewnętrzna część cegły) i ciecz immersyjna (woda/parafina) są czynnikami, które znacząco oddziałują na wyniki oznaczania BD i oPo. Z drugiej strony stwierdzono, że materiał użyty do usuwania wody z powierzchni próbki, czas usuwania i czasu zanurzenia w wodzie w otaczających warunkach nie wypływały na wyniki oznaczenia BD i oPo. Drugi plan doświadczeń, który obejmował cztery najważniejsze czynniki, został przeprowadzony w przypadku tego materiału ogniotrwałego w czterech różnych laboratoriach. W ten sposób otrzymano oznaczenia powtarzalności i odtwarzalności norm badania w różnych laboratoriach w przypadku BD i oPo. W przypadku normy EN 993-1 testowanej na korundowym, gęstym, formowanym materiale ogniotrwałym (nie reagującym z wodą jako cieczą immersyjną) w przypadku BD otrzymano odtwarzalność 0,07 g/cm^3 i powtarzalność 0,04 g/cm^3, natomiast w przypadku oPo – odtwarzalność 1,6% obj. i powtarzalność 1,2% obj.

Słowa kluczowe: gęstość pozorna, porowatość otwarta, badanie, formowane materiały ogniotrwałe, odtwarzalność

1. Introduction

The testing standard EN 993-1 for dense shaped refractories, which describes the BD and oPo testing methods for this refractory material, includes up to 15 factors (for example the factors quoted in table 1 including also factors not explicitly described in the testing standards, e.g. the way of wringing the cloth in order to have it saturated with immersion liquid, the influence of the temperature of the immersion liquid coming into contact with the sample at the beginning of the test, the time that a sample remains in a desiccator after having been dried at 110°C, the position of the samples in the airtight vessel...) which can vary significantly among different laboratories. A more precise definition of these factors will lead to improved accuracy and precision of the results of BD and oPo testing and thus make the results more comparable. A conventional method to identify the significant factors that influence the results of a testing method is to vary one factor for each experimental run while keeping all other factors constant. This method is very expensive and time consuming and fails to determine the combined effect of multiple factors on the testing result. That is why A number of factorial designs have been used to address these problems [1]. Among these, full factorial designs provide more complete information, but this method requires numerous experiments (L^k experiments, where k is the number of factors and L is the number of levels for each factor). This makes full factorial designs impractical if a large number of factors have to be studied. However, screening designs (fractional factorial designs) offer an effective and economic means to analyse such large numbers of factors using a minimum number of experiments.

Plackett-Burman design (PBD) [2] is the most frequently used screening design because of its ability to estimate all main effects (calculated as the difference of the mean results of a number of tests with different levels of a particular factor) with the same precision. The main effect of each response is evaluated as the difference between averages of measurements made both at the high level (+1) and the low level (-1) of each factor. It is a fractional factorial design with the advantage of minimising the experimental runs, finding the most significant factors from a large number of factors. Using this design, k factors can be screened with k+1 experimental runs. In this study, the most significant factors which affect the accuracy and the precision of the testing method for the determination of BD and oPo according to the testing standard EN 993-1 for dense shaped refractories were determined. After the identification of the most significant factors that influence the testing results when testing this different materials, a second design of experiment which contained the four most significant factors was studied in four different laboratories in order to obtain an estimation of the repeatability and of the reproducibility of the testing standard between laboratories.

2. Material and methods

2.1. Refractory material description

The high alumina product type HA75 ISO 10081-1 was a bauxite dense shaped refractory product produced by RHI AG for the need of the EU project “ReStaR”. It contains mainly Al_2O_3 (81.0 wt.%), SiO_2 (13.0 wt.%), TiO_2 (3.2 wt.%) and Fe_2O_3 (1.7 wt.%) (EN ISO 12677). The material has a BD of 2.75 g/cm^3 (EN 993-1), an apparent porosity of 20.5% (EN 993-1) and a cold crushing strength of 70.0 N/mm^2 (EN 993-5) according to the data sheet.

2.2. Evaluation of the error of the testing equipment

The uncertainty of the testing equipment used in the scope of this investigation was evaluated for each material in order to know the level of confidence of the results and its quality. For this the software GUMsim was used. The algorithms involved are based on the current international principles/instructions of DIN/ISO/BIPM Guide to Expression of Uncertainty in Measurement (GUM) [6, 7]. In the case of the investigated testing methods for BD and oPo, the uncertainty of the testing equipment is based on the propagation on the uncertainty of the weighting for each step of the testing procedure and on the uncertainty of the density of the immersion liquid, which depends of the temperature. It was found that the error of the testing equipment used in the scope of this investigation to measure BD was ±0.002 g/cm^3 and error of the testing equipment to measure oPo was 0.01 vol%.

2.3. Fractional factorial design

The fractional factorial design method was used to evaluate the relative importance of various factors on the bulk density and open porosity testing results according to the mentioned standard.

For the standard EN 993-1 studied with the HA75 dense shaped refractory, a total of sixteen factors were identified. The independent factors and their levels are shown in Table 1. The selected levels of investigation are fixed at high (+) and low (-). The responses are the bulk density (BD) and the open porosity (oPo). The experimental design analysing the fifteen factors at two levels was composed of 16 runs (16 different experiments) and the experiments were again replicated four times. Furthermore, the experimental design was replicated two times, the first time with water and the second time with Puretol as immersion liquid, i.e. each sample was first tested with water as immersion liquid and then with Puretol as immersion liquid.

2.4. ANOVA analysis of the factorial design

Analysis of variance (ANOVA) [8] is an analysis of the variation present in an experiment. It is a test of the hypothesis that the variation in an experiment is no greater than that due to normal variation of individual characteristics and error in the measurement. The tests in an ANOVA are based on the F-ratio: the variation due to an experimental effect divided by the variation due to experimental error. This ratio is equal to 1.0 if the experimental effect is the same as the experimental error. If the F-ratio is significantly large and the subsequently obtained p-value is lower than 0.05 then the factor is considered statistically significant. The statistical significance (p-value) of a factor represents a decreasing index of the reliability of a result. The higher the p-value, the less we can believe that the factor is statistically significant on the results. Specifically, the p-value represents the probability of error that is involved in accepting the observed result as valid. Historically, a threshold value of 0.05 is often assumed to determine a significant effect of a factor on the testing results.

2.5. Round Robin Test

A round robin test is an interlaboratory test (measurement, analysis or experiment) performed independently sev-

Table 1: Factors and levels used for the evaluation of the standard EN 993-1 studied with the HA75 dense shaped refractory.

Factor	Label	Low Level (-)	High Level (+)
Operator	*Op*	Operator 1	Operator 2
Waiting time under vacuum before filling with the immersion liquid	*Tvac* [min]	15	30
Vacuum level	*Vac* [Pa]	2500	3500
Waiting time after filling with the immersion liquid under vacuum	*Wp* [min]	30	45
Waiting time after filling with the immersion liquid and under atmospheric pressure	*Wwp* [min]	30	45
Sponging material (cloth, towel)	*Sp*	linen	leather
Geometry of the samples	*Geo*	Prism	Cylinder
Immersion liquid	*Liq*	water	Paraffin (Puretol)
Temperature of the immersion liquid coming into contact with the sample	*Temp* [°C]	15	30
Waiting time in a desiccator of the test piece after having been dried at 110°C in the drying chamber	*Texi* [h]	Necessary time to reach the room temperature	24
Position of the samples in the airtight vessel	*Pos*	Under (1st level)	Up (2nd level)
How to wring the cloth/towel saturated by the immersion liquid	*Wr*	Wring the cloth/towel	Sin-dry with a roller
Press direction of the samples	*Press*	Cut or drilled in the press direction	Cut or drilled perpendicular to the press direction
Place of extraction of the samples from bricks	*Bp*	Center of the brick	Side of the brick
Volume of the sample	*Vol* [cm^3]	50	200

eral times. In the scope of this investigation, four laboratories throughout Europe performed the same testing methods (measurement of the BD and the oPo on refractory materials according to EN 993-1) on the same materials but with different equipment. The aim of the round robin test is to determine the reproducibility and the repeatability of the testing methods, applied to determine the properties of refractory as described.

The repeatability was defined as the closeness of agreement between independent results obtained with the same method on identical test material under the same conditions (same operator, same apparatus, same laboratory and after short intervals of time). The reproducibility was defined as the closeness of agreement between independent results obtained with the same method on identical test material but under different conditions (different operators, different apparatus, different laboratories and/or after different intervals of time).

In the round-robin test the influence of the ration of the longest to the shortest dimension of the samples (*L*/*d*: (-) 1; (+) 1,5), of the kind of sponging material (*Sp*: (-) linen; (+) leather), of the time of vacuum pressure (*Tvac*: (-) 15 min; (+) 30 min) and of the time that the sample is immerged in the immersion liquid after the vacuum pressure has been removed (*Wwp*: (-) 30 min; (+) 45 min) on the BD and oPo testing results was analysed. Furthermore the effect of the position of the extraction of the samples from bricks (*Bp*) was analysed. Thus, for each run of the factorial design, three samples were extracted from the border of a brick and for each run one sample was extracted from the middle of a brick. Other parameters were kept at fixed levels (*Vac* to 2500 Pa and *Wp* to 30 min). In order to reduce the standard deviation between the results of different laboratories, only water was used as immersion liquid for the tests. The four influencing factors quoted previously were tested in five different laboratories in order to determine the most significant factors influencing the BD and oPo testing results of dense shaped refractory material and in order to obtain an estimation of the repeatability and of the reproducibility of the testing methods and results. For each run, each laboratory used four different samples and each sample was tested only once (Table 2).

Table 2. The Round Robin Test Factorial Design Matrix for the standard EN 993-1 studied with the dense shaped refractory HA75.

Run N°	*L*/*d*	*Sp*	*Tvac* [min]	*Wwp* [min]
7	1.5	leather	30	45
1	1.5	leather	15	30
3	1.5	linen	30	30
8	1.5	linen	15	45
2	1	linen	15	30
4	1	linen	30	45
6	1	leather	15	45
5	1	leather	30	30

3. Results

3.1. Fractional factorial design

The 15 factors shown in Table 1 were examined using a fractional factorial design. The main effects (effect of a single independent variable on a dependent variable – ignoring all other independent variables.), F-ratios and the p-values were calculated for the BD and oPo testing results as described before. A p-value of less than 0,05 for four factors *Bp*, *Liq*, *Geo* and *Wwp* indicated that these factors are statistically significant for the BD testing results. Likewise, the factors *Bp*, *Wwp*, *Tvac* and *Vol* were found to be statistically significant for the oPo testing results.

The influence of the place of extraction of the samples (internal or external part of the brick, *Bp*) on the BD testing results was found to be significant. A higher BD result and lower oPo result were obtained when the sample had been extracted from the middle of a brick. Furthermore lower BD testing results were obtained with Puretol than with water as immersion liquid (*Liq*). The BD testing results were also found to be higher for a small sample geometry (*Geo*). Moreover the waiting time with the immersion liquid and under atmospheric pressure (*Wwp*) increased the BD testing results and their standard deviation and decreased the oPo results when the waiting time was increased.

3.2. Round-Robin Test

First, in order to determine only the error due to the factors by avoiding the addition of the error due to the inhomogeneity of the material, the same samples were tested for each run of the factorial design (Table 2) in one laboratory (at Forschungsgemeinschaft Feuerfest e.V. in Germany). Four samples with the ratio L/d =1 and four samples with the ratio L/d = 1,5 were tested. As results of these two factorial designs it was noted that the maximum standard deviation of the BD testing result from one sample is 0.003 g/cm^3 and the maximum standard deviation of the oPo testing result is 0.1 vol%, which was considered to be very low. The testing results of five independent laboratories throughout Europe were then collected in one factorial design and analysed using the software OptiVAL as described before. For each run of the factorial design, testing results from testing of 20 samples were analysed (four from each laboratory). From the analyses it was found that:

– A general deviation of the testing results between the laboratories was present due to a problem of heterogeneity of the bricks.

– The factor *Sp* was found not to significantly affect the testing results but a worse repeatability was observed when the leather towel was used. Thus, the use of the linen towel as sponging material is recommended.

– The factor *Tvac* was found not to significantly affect the testing results. Thus a waiting time of 15 min is deemed enough.

– The factor L/d was found not to significantly affect the testing results.

– The factor *Wwp* was found not to significantly affect the testing results. So a waiting time of the sample in immersion in liquid under atmospheric pressure of at least 30 min is deemed enough.

Another calculation was made to analyse the influence of the position where samples are extracted from a brick (results obtained from samples extracted from the side of a brick and results obtained from samples extracted from the centre of a brick, Table 3). The results showed that the standard deviation is lower if the tested samples are extracted from the centre of a brick. The BD was found to be higher and the oPo lower when obtained from samples from the centre of a brick.

Utilising the software PROLab from Quodata, a statistical analysis of the round-robin test was carried out. It was noted that there were only small differences in the results between all runs (Table 2) for the reproducibility and the repeatability of the testing methods. Thus, for a practical issue, the combination of factors as used for the run number 2 is recommended. That is when samples with a ratio L/d of 1 are being used, the waiting time under pressure without liquid is being fixed to 15 min, the samples are kept at least 30 min immersed in water under atmospheric pressure, and the excess water is removed using a saturated linen towel. A reproducibility of 0.07 g/cm$_3$ and a repeatability of 0.04 g/cm3 for the BD and a reproducibility of 1.6 vol% and a repeatability of 1.2 vol% for the oPo can then be obtained.

Table 3. Comparison of the results and the standard deviation of the results for the BD and the oPo testing from samples extracted from the side or from the centre of dense shaped refractory HA75 bricks (SD = standard deviation).

	BD [g/cm^3]	BD SD [g/cm^3]	oPo [vol%]	oPo SD [vol%]
All samples	2.73	0.02	20.2	0.5
From the side	2.73	0.02	20.3	0.5
From the centre	2.74	0.01	20.0	0.3

4. Discussion

Recommendations can be given to achieve high reproducibility and high repeatability of the BD and oPo testing methods concerning refractory materials.

For the involved testing standard, it can be applied that:

– The time waited under vacuum before filling with the immersion liquid should be at least 15 min.

– The waiting time with the immersion liquid under vacuum should be 30 min.

– The waiting time with the immersion liquid and under atmospheric pressure should be at least 30 min.

– The vacuum pressure should be set to 2500 Pa. A lower vacuum pressure will increase the standard deviation of the testing results between results obtained in different laboratories. If water is used as immersion liquid, its temperature should be held below and/or equal to 20 °C in order to attain the maximum vacuum pressure of 2500 Pa. It is recommended to always wait until the water boils to ensure the maximum vacuum is attained for a given temperature.

Table 4. Summary of the reproducibility and repeatability obtained for the standard EN 993-1 for dense shaped refractory.

Standard EN 993-1 using the dense shaped refractory HA75	Reproducibility		Repeatability	
	Best combination	Worst combination	Best combination	Worst combination
BD [g/cm^3]	0,07	0,07	0,04	0,05
oPo [vol%]	1,6	1,9	1,2	1,3

– The time that a sample should be placed in a desiccator after having been dried at 110 °C in order to cool down (*Texi*, between 2 hours and 24 hours) showed no significant impact on the testing results. The current testing standards suggest placing the test piece in a desiccator until it has cooled to room temperature. As no significant impact of the waiting time on the testing results were found, in order to save time, the samples can be put in the desiccator at the end of the day before being tested the next morning for example. The position of the samples in the airtight vessel showed no significant impact on the testing results. The whole vessel with several layers of samples can be used to study the BD and the oPo without significant effect on the testing results.

A linen towel should be chosen as sponging material, as using a leather towel resulted – in some laboratories – in a higher standard deviation of the oPo and BD testing results. One main reason is thought to be that the leather towel showed some difficulties to store a constant level of moisture. Cylinders with a format of 50 mm x 50 mm can be chosen as this is the standard geometry for Cold Crushing Strength. Despite a lower standard deviation was found if the samples are extracted from the centre of the brick, it is not possible to privileged the position of extraction of the samples. That is why the samples should be extracted randomly from bricks. The side or the centre of the brick shall not be privileged, as an inhomogeneity between both locations may exist due to the pressing process of bricks.

Whenever possible, the immersion liquid should be water in order to reduce the standard deviation between results from different laboratories.

5. Conclusion

Factorial designs for the testing standards EN 993-1 for dense shaped refractory were effectively applied for the screening of the factors that influence the results of the BD and the oPo testing results on these refractories. A second design of experiment which contained the four most significant factors was studied for this testing standard in five different laboratories throughout Europa to evaluate precisely the effects and possible interactions of the influencing parameters/factors and estimate the repeatability and the reproducibility of this standard, which are summarised in the Table 4.

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