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Hot-erosion of nano-bonded refractory castables for petrochemical industries

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Abstract

Cold-erosion tests are usually applied for refractory castable evaluation in petrochemical industries, mainly for materials used in cyclones and risers of fluidized catalytic cracking units (FCCU). Due to the fact that in the operation, the refractory material is subjected to high temperature, at first, hot-erosion tests could be more representative. Erosion wear has a great influence on the FCCU refractory working life and the lost income associated with a production halt can reach values close to US$500,000 per day. These aspects are strong enough to justify hot-erosion resistance characterization. The test viability, which could result in selecting better material for the application, was evaluated using commercial products and nano-bonded castables from 200 up to 815 °C. At this temperature range, a significant difference between the cold and hot-erosion loss was not observed. Therefore, it indicates that the cold-erosion test is suitable and sufficient for selecting refractory castables for FCCU applications. The cold-erosion test also presented a higher data correlation with the splitting tensile strength and the hot modulus of rupture. Regarding the different evaluated materials, the nano-bonded castables showed a higher erosion resistance and were less susceptible to the temperature effect than the calcium aluminate cement bonded commercial products.
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Keywords: Petrochemical industry; Hot-erosion; Nano-bonded castables

1. Introduction

High erosion resistance is a key property for refractory castables applied to cracking units of petrochemical industries. Usually measurements are taken at room temperature (cold-erosion) using pre-fired samples that are subjected to the erosive action of SiC particles under a perpendicular impact angle (ASTM C 704). Nevertheless, testing at high temperatures could be more suitable for the erosion resistance evaluation, as it is closer to the working conditions. It is reasonable to propose that the erosion of materials tested at room and high temperatures will show distinct behavior. Firstly, because with the temperature, the material can better absorb a part of the erosive particles impact energy. Secondly, the glassy phase at the grain boundaries can make this region less prone to brittle fractures [1]. Considering the cracking unit (FCCU) petrochemical environment, the main interest is to evaluate erosion resistance at temperatures below 900 °C. The literature presents no clear trends regarding hot-erosion results. For different aluminas that were pressed and fired at 1550 °C for 2 h, Zhou and Bahadur [1] observed an increase in the erosion rate from 400 °C to 800 °C. In a recent study [2], no changes in the erosion rates were detected for alumina based refractory bricks tested under an impact angle of 90° and temperatures up to 1000 °C. Only at 1200 and 1400 °C, a reduction of the erosion rate was observed. Nevertheless, as the SiC particles were stuck on the sample's surface at 1400 °C, leading to negative values of the erosion rate, the results at this test temperature were not considered. Additionally, the effect of the impact angle was evaluated at room temperature and at 1200 °C. The erosion rate increased with the impact angle

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for the cold condition and the maximum wear rate was close to 90°. This is typical behavior for brittle materials due to the higher impact energy on the sample's surface at a perpendicular angle [3]. At 1200 °C, one of the refractory materials tested presented the highest erosion rate at 60°, whereas the others were at 90°. Therefore, the information available in the literature is scarce and not enough to ensure that high temperature-erosion tests are necessary for the characterization of petrochemical materials. Because erosion wear resistance is a key issue for this application, an evaluation using different materials is required to define whether or not hot-erosion tests can help the refractory selection process. In this context, calcium aluminate cement bonded commercial products for the fluid catalytic cracking unit (FCCU) and a novel generation of nano-bonded castables [4–7] were submitted to the hot-erosion test for the impact angle of 90° and temperatures of 200, 400, 600 and 815 °C. As this test is not standardized and there is no commercial equipment available, a hot-erosion device was built up. The accuracy of the equipment for hot measurements was checked at room temperature comparing the results to those attained using a commercial and standardized one (ASTM C 704).

2. Experimental

Nano-bonded refractory castables containing tabular alumina, mullite grog or fused silica were designed according to Alfred's packing model ($q=0.24$–0.26) [8]. Tabular alumina ($D_{max} \leq 6$ mm, Almatis, Germany) and mullite grog ($D_{max} \leq 6.73$ mm, CE Minerals, USA) compositions comprised 85.5 wt% of the aggregates for each composition. In these systems, 2.5 wt% of sintering additives, consisting of a mixture of Al powder and a light element-based compound (under patent application), were added. The silica castable composition contained 70 wt% of fused silica ($D_{max} \leq 4.75$ mm, CE Minerals, USA), 16 wt% of tabular alumina (−0.2 mm, Almatis, Germany) and 1 wt% of sintering additives. The matrix of the three refractory systems comprised 10 wt% of reactive alumina (CL370C, Almatis, Germany) and 2 wt% of fumed silica (MS971, Elkem, Norway). Aqueous colloidal silica suspension (40 wt% solid content-Bindzil 1440, Eka Chemicals, Sweden) was selected as a binding agent for the tabular alumina and fused silica based castables. The suspension content added was determined to attain castables with 60% of vibratable-flow (ASTM C 680). Therefore, 7 wt% of the colloidal silica suspension for the high-alumina material and 8.7 wt% for the silica one were added. The particle size distribution for the mullite grog based castable was designed to result in self-flow behavior. In order to attain 60% of free-flow, 13 wt% of a colloidal silica suspension (50 wt% of solid content-Bindzil 50/80, Eka Chemicals, Sweden) was added. The commercial products evaluated (A, B and C; Table 1) were calcium aluminate cement bonded refractory materials used by the Brazilian petrochemical industry for the FCCU application.

Product A is an 88 wt% alumina plastic refractory material for hexagonal mesh application in cyclones for FCCU's reactor and regenerator. Product B is a self-flowing bauxite based castable and C an alumina–silica vibratable one, both for riser lining application. Moulding was performed using the water content shown in Table 1, which is in agreement with the producer data sheet. A nano-bonded and commercial product mixing process was carried out in a rheometer especially developed for refractory castables [9]. After shaping, the colloidal silica bonded castables were cured at 50 °C for 24 h in an unsatured environment (without humidity) [10]. The cement-containing one, was cured in an acclimatized chamber (Vötsch 2020, Germany) at 50 °C and with 80% relative humidity. The drying step was carried out at 110 °C for 24 h and firing conducted under a heating rate of 3 °C/min and 5 h of dwell time at 200, 400, 600 or 815 °C. The latter temperature was selected to be used as a common reference for the petrochemical industry materials. The castables were characterized using the following tests: splitting tensile strength, hot modulus of rupture and erosion resistance at room (cold) and hot temperature. Splitting tensile strength (ASTM C 496-90) was measured using an MTS Systems equipment (Model 810, USA) using 40 mm × 40 mm cylindrical samples. For the hot modulus of rupture (ASTM C 583-8), prismatic samples of 150 mm × 25 mm × 25 mm were tested in a HBTS 422 equipment (3-point bending test; Netzsch, Germany) using a loading rate of 12.5 N/s. The cold-erosion resistance (ASTM C 704) was evaluated (1 kg of no. 36-grit silicon carbide to erode samples of 115 mm × 115 mm × 25 mm) using a NBR 13185 apparatus (Solotest, Brazil), according to Fig. 1. In this equipment, SiC erosive particles are

Table 1
Commercial products characteristics.

Characteristic	Commercial A	Commercial B	Commercial C
Chemical analysis (wt%)			
Al_2O_3	88.0	62 min	45.8
SiO_2	8.0	35 max	49.9
CaO	2.0	[a]	[a]
Apparent density (g/cm^3)	2.85	2.50	2.27
Water content (wt%)	4.8	6.5	7.0

[a]Not informed by the producer.

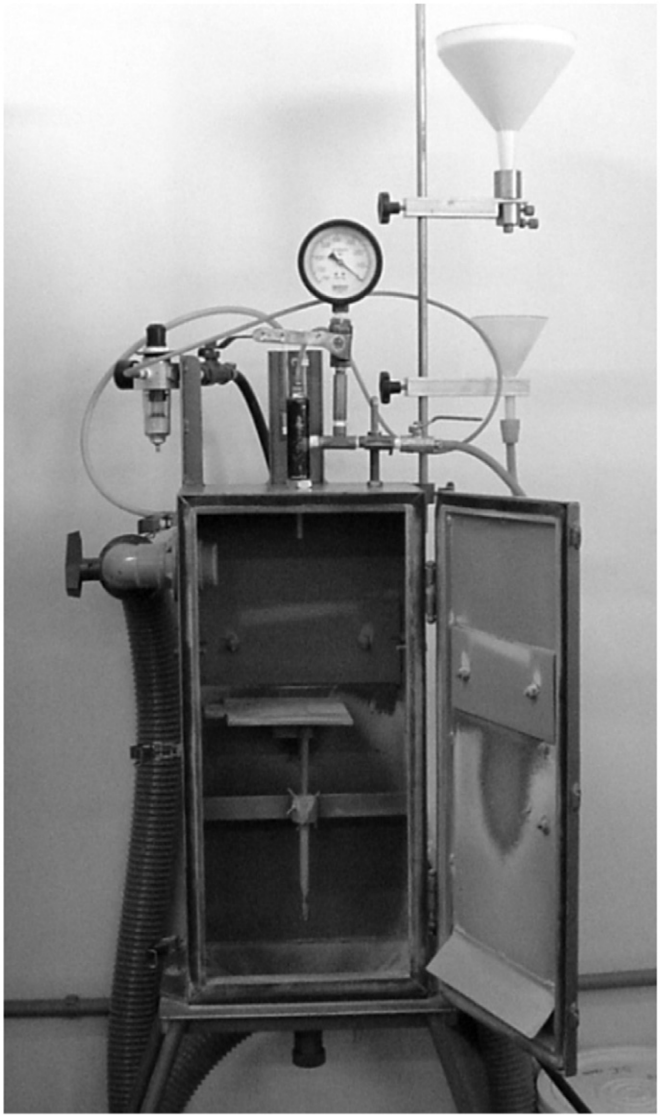

Fig. 1. Equipment for cold-erosion test (ASTM C 704).

Fig. 2. Designed equipment for hot-erosion evaluation.

conveyed by air flux and hit the sample's surface placed at 90° regarding the particles flow. The material loss was expressed in terms of eroded volume (ΔV), using the following equation:

$$\Delta V = \frac{M_i - M_f}{M_{ea}} \quad (1)$$

where, ΔV is the material volumetric loss after the test (cm^3), M_i and M_f (g) are, respectively, the initial and final mass of the sample and M_{ea} the specific apparent gravity (g/cm^3).

The hot-erosion test was carried out in an equipment designed and built by the authors, according to Figs. 2 and 3.

The test starts with the injection of compressed air in the preheating unit that can reach 1000 °C. In this furnace, four vertical mullite tubes are heated by electrical resistances. In the inner part of each of these ceramic tubes, another one with the same composition is used for heating the air. Afterwards, the hot air is guided to a nozzle where SiC particles are forwarded to the sample testing furnace through a feeding tube. The bottom furnace is a stainless steel chamber lined with ceramic fiber plates which can be heated up to 1000 °C, allowing carrying out tests on four samples successively. The hot-erosion tests were performed using the same set of conditions as used for the cold-erosion one, such as: SiC specification, impact angle of 90°, distance between the sample and the nozzle and the testing time. Due to the dimensional differences between the equipment components, it was not possible to use the same air pressure. Therefore, calibration of the hot-erosion equipment was required to define the pressure that would enable the same erosion loss value when tested in the cold-erosion equipment at room temperature. For these calibrations at room temperature, standard glass plates were used, due to the high reproducibility of their erosion values. For the hot-erosion evaluation, pre-fired samples at the testing temperature were placed at the bottom furnace and heated up to the set temperature. After this preheating stage, the pressure was adjusted when the temperature reached a constant value. Because the SiC erosive particles were not previously heated, during the initial testing steps a decrease of roughly 20 °C in the

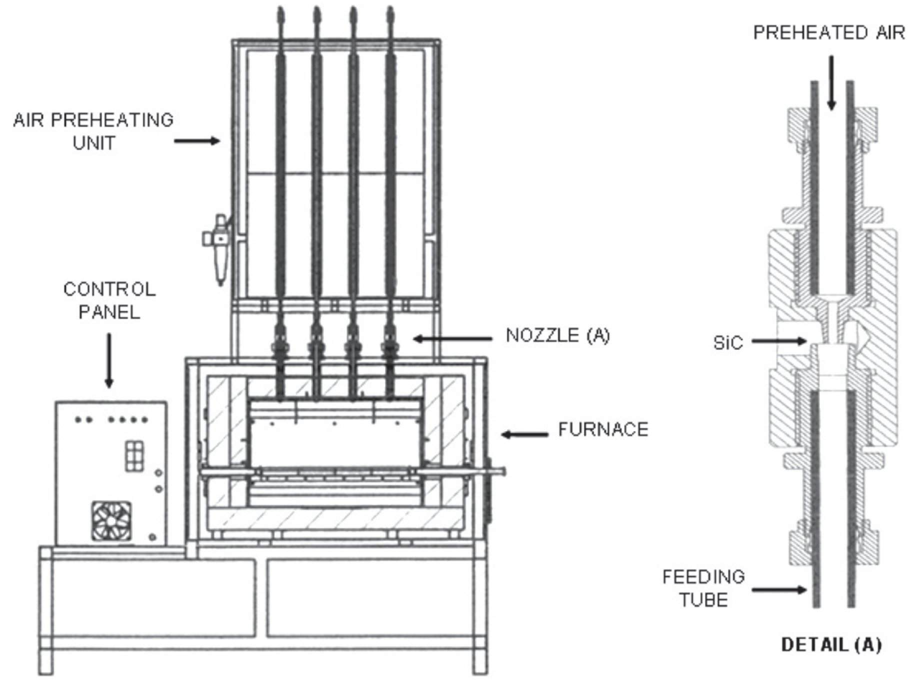

Fig. 3. Components of the hot-erosion equipment.

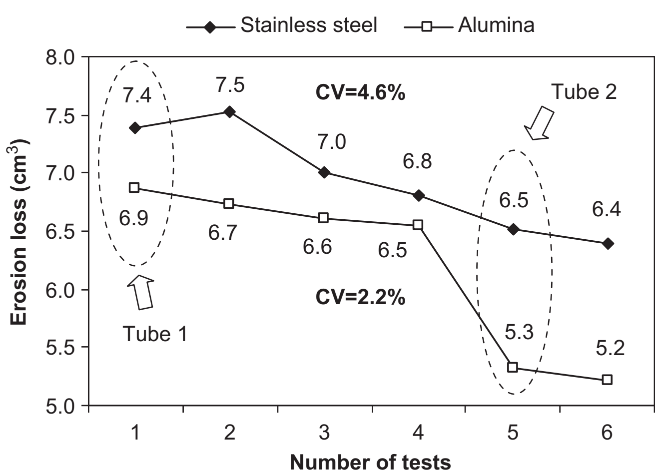

Fig. 4. Calibration results using stainless steel AISI 310 and alumina feeding tubes.

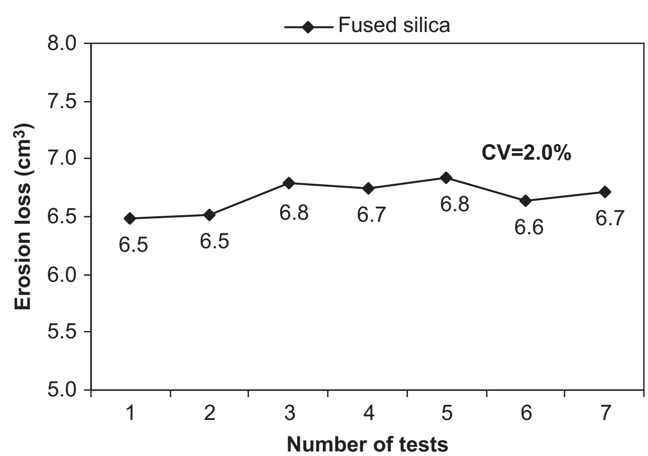

Fig. 5. Calibration results using fused silica feeding tubes.

temperature was detected which was quickly reduced afterwards. After cooling down, the samples were withdrawn and the erosion loss was calculated according to Eq. (1). The feeding tube (Fig. 3) was replaced after each test due to the wear caused by the SiC particles.

3. Results and discussion

3.1. Hot-erosion equipment calibration features

Because there is no standard for hot-erosion tests, it was decided that the equipment should be calibrated at room temperature using soda–lime glass plates. As previously mentioned, the air pressure was adjusted to result in the same erosion loss value as in the cold-erosion equipment. Nevertheless, due to the natural wearing of the feeding tube that conveys the SiC (Fig. 3), it was possible to certify that the initial calibration would not remain for subsequent tests using the same tube. This aspect was detected for tests using stainless steel AISI 310 and alumina tubes, two materials that would firstly come to mind to withstand such a demand. Fig. 4 shows the calibration results considering four consecutive tests with the same tube (tube 1) and its replacement for a new one (tube 2). Because the air pressure was constant, different values of erosion loss were associated to the inner diameter differences of the two tubes.

During the four tests, the inner diameter increased changing the particle's velocity and leading to a substantial reduction in the erosion loss. For the stainless steel AISI 310 tube, the behavior was more significant due to the higher coefficient of variation (CV) attained, which is defined as the standard deviation of the values divided by standard deviation of the mean. After replacing tube 1 for tube 2, the new values of erosion loss were very different. Analyzing the stainless steel AISI 310 and alumina tubes' dimensional specifications for the inner diameter, it was detected that they were not constant even before using. Therefore, there was no confidence that tubes of the same batch could lead to similar results. In this situation, the test would be useless due to the lack of reproducibility. In order to solve this problem fused silica tubes, which presents better dimensional tolerance and stability up to 1000 °C, was used and replaced after each test. Fig. 5 shows the calibration results using the fused silica tubes.

The reproducibility was much better than that observed for stainless steel AISI 310 and alumina tubes, leading to higher reliability.

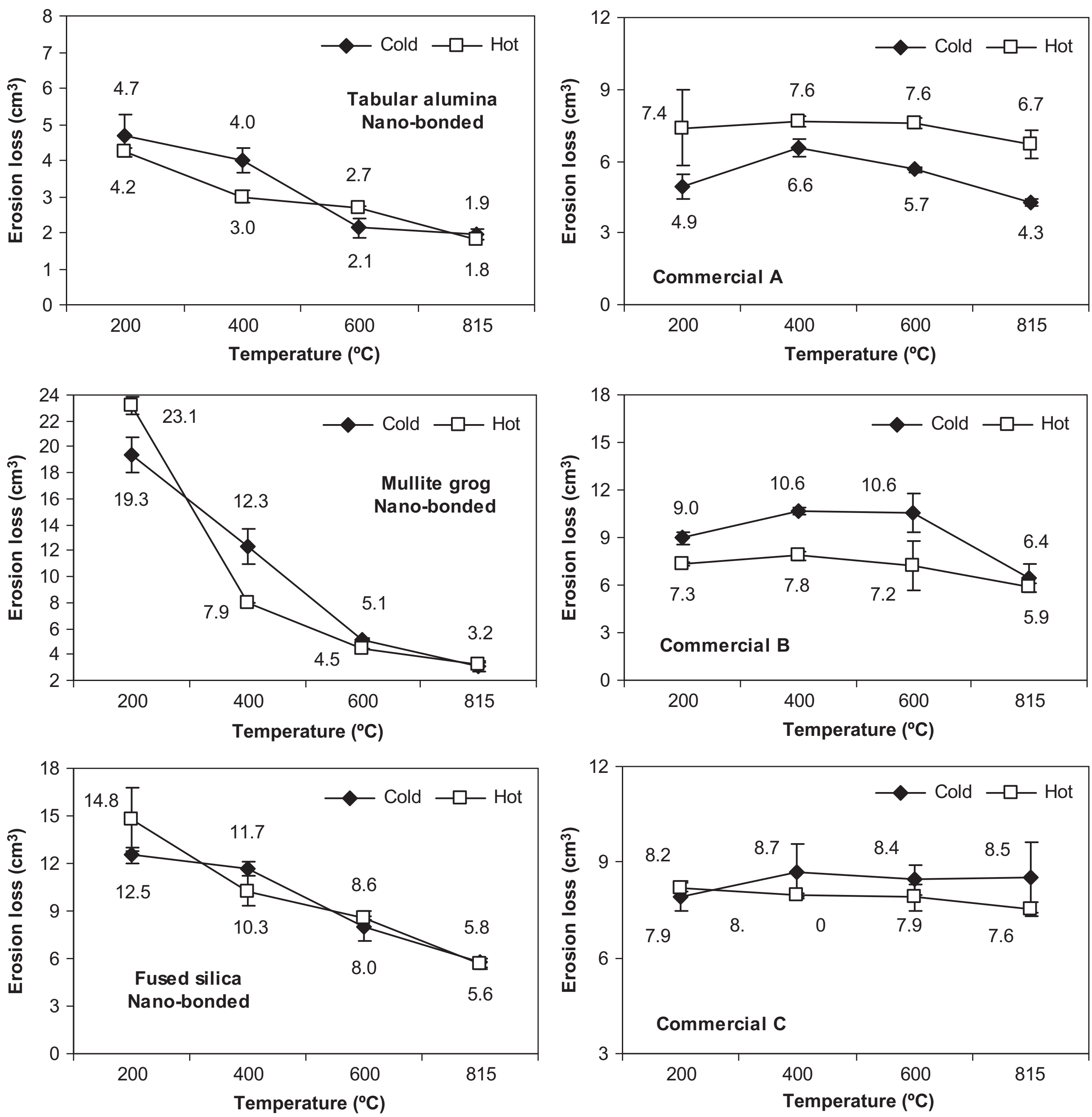

Fig. 6. Commercial products and nano-bonded castables erosion resistance.

3.2. Commercial products and nano-bonded castables evaluation

Fig. 6 shows the results of hot and cold-erosion loss for commercial products and nano-bonded castables.

For the cold and hot-erosion, the nano-bonded castables showed a great erosion loss reduction with the testing temperature increase, whereas the commercial products presented distinct behavior. When calcium aluminate cement is used as a binder agent, a considerable increase in erosion resistance is not observed with the temperature due to the hydrate decomposition up to 600 °C and the low sinterability below 1000 °C [11]. The results obtained for the cold and hot-erosion tests were close for all nano-bonded materials and commercial product C. For product A, the hot-erosion was higher than the cold one, whereas an opposite behavior was observed for product B. A clear explanation for these results was not found due to little information about the commercial products, although the trend of the attained values are similar with the temperature. The data correlation between hot and cold-erosion for all evaluated materials and temperatures is shown in Fig. 7.

A correlation index value of 0.81 was observed by linear data fitting and the resulting equation was very close to $y=x$, indicating that in the range between 200 and 815 °C, there was no significant difference between the hot and cold-erosion for the evaluated materials. The correlation was even higher for the nano-bonded castables (Fig. 8), indicating that they are less sensitive to the temperature effect.

Based on these results cold-erosion tests showed, in general, to be reliable to evaluate refractory materials for petrochemical industries. Thus, there might be no need for the hot-erosion tests, which are more complex and much more expensive due to the materials used in manufacturing the equipment. Nevertheless, the effect of temperature cannot be disregarded, but can be estimated using indirect measurements. Therefore, one important aspect was to check the correlation between the erosion wear and the

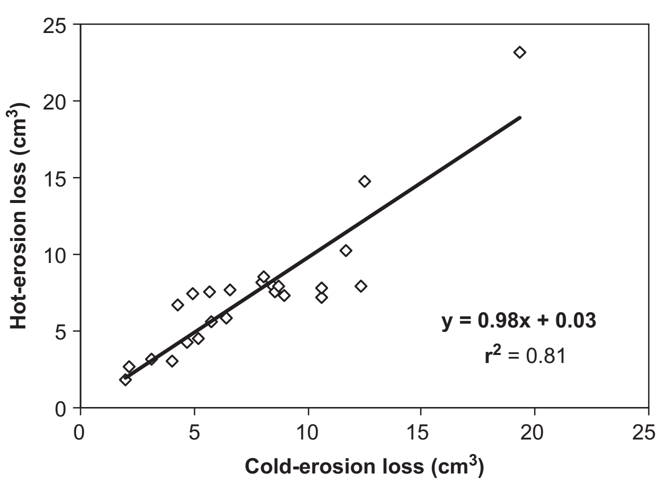

Fig. 7. Hot and cold-erosion results correlation for the commercial products and nano-bonded castables.

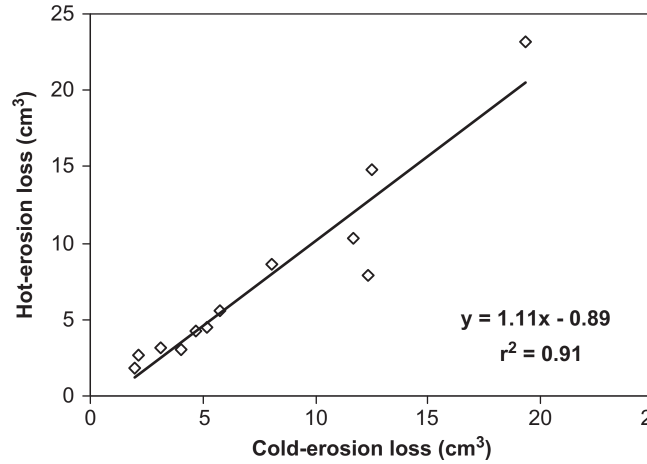

Fig. 8. Hot and cold-erosion results correlation for the nano-bonded castables.

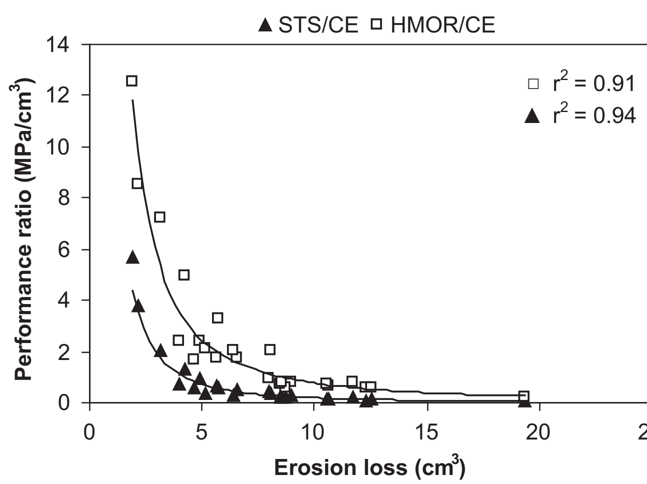

Fig. 9. Correlation between splitting tensile strength (STS) or hot modulus of rupture (HMOR) and cold-erosion loss (CE) results.

mechanical strength, as the results can be used to forecast the refractory performance. Fig. 9 shows the data correlation between splitting tensile strength or hot modulus of rupture and the cold-erosion loss by using a performance ratio. The same comparison was carried out for the hot-erosion values presented in the Fig. 10.

The cold-erosion test showed better correlation with the mechanical strength measurements, attesting that cold-erosion resistance instead of the hot one, could be sufficient to evaluate the most refractories applied in FCCU.

4. Conclusions

The characterization of commercial products and nano-bonded castables for FCCU application using hot and cold-erosion tests for the temperature range between 200 and 815 °C, showed no significant difference in the erosion loss results and trends for these two tests. This is a clear indicative that the cold-erosion test might be sufficient to evaluate the erosion resistance of castables for petrochemical industries.

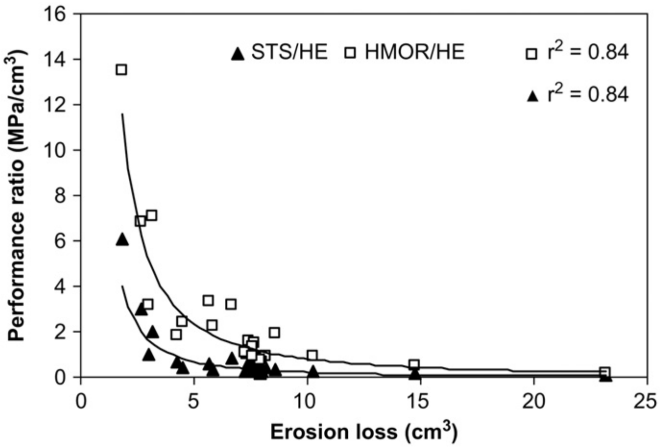

Fig. 10. Correlation between splitting tensile strength (STS) or hot modulus of rupture (HMOR) and hot-erosion loss (HE) results.

Additionally, the cold-erosion resistance presented a better correlation with the splitting tensile strength or hot modulus of rupture tests. Among the tested castables, the nano-bonded showed a higher erosion resistance and less sensitivity to the temperature effect.

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