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Statistical analysis of compressive strength data of ceramic Raschig rings fabricated by an extrusion process using a Weibull distribution

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The influence of sintering conditions on the reliability of a special ceramic packing namely a Raschig ring, was investigated. The special kaolin used in the industrial ceramic Raschig rings manufacturing process was shaped by an extrusion method and sintered at 1200 and 1250°C using different soaking times, ranging from 30 to 180 minutes. The physico-chemical properties of specimens such as shrinkage, water absorption, bulk density, porosity, microstructure and mineralogical composition, were studied. According to the obtained results, the best sintering conditions were determined. The diametrical compressive strength of fired samples was measured on suitable specimens. The differences found in the strength data were evaluated using Weibull theory. The statistical results show that the maximum Weibull modulus is obtained when ceramic Raschig rings are fired at a lower sintering temperature and longer soaking time to reach the minimum total porosity. However, the soaking time needs to be optimized to realize the maximum strength and reliability during the fabricating process at a given temperature.

Key words: Ceramic Raschig rings, Compressive strength, Weibull modulus.

Introduction

Packed columns are widely used in chemical and petrochemical industries to contact two phases. They were used in chemical processes such as catalytic reactions, combustion, gas absorption, distillation and separation processes. The most important part of a packed column is the tower packing. Ceramic packings are fabricated in different geometrical shapes. The Raschig ring is the oldest regular ceramic packing with the simplest hallow cylindrical shape that is still used today for many applications. It is characterized by equal height and external diameter of the packing element [1-3].

The required technical performance of conventional ceramic packings is normally associated with their water absorption, porosity and chemical stability [2, 3]. These characteristics largely determine the mechanical properties and performance of ceramic packings. The compressive strength of ceramic Raschig rings is one of the important key parameters for the reliable performance of packed columns. Ceramic Raschig rings with a low compressive strength may break in packed columns and this phenomenon causes various operational problems for industrial units such as blockages and an increase in pressure drop [1, 2].

At an industrial scale, ceramic Raschig rings are fabricated by three methods which are extrusion, uniaxial pressing and slip casting. The extrusion process is the most reliable method for shaping ceramic Raschig rings [4]. The raw materials used in the production of ceramic Raschig rings are generally kaolin and/or kaolinitic-illitic clays with a very low iron oxide content, which is essential to develop plastic forming and provide the desirable mechanical strength for both the green and dried body pieces [5, 6]. A fluxing agent such as feldspar may also be used in the composition of the ceramic packing but these are non-plastic materials and decrease the plasticity. During the sintering process, a liquid glassy phase is formed. The viscosity of the liquid phase decreases significantly, as the temperature rises. This phenomenon allows the liquid phase to flow into the pores of the body and eliminate them, progressively. Indeed total porosity is affected by two factors [7]: (i) the capillary pressure, due to the surface tension of the liquid phase which tends to reduce open and total porosity with a cocurrent increase in linear shrinkage: (ii) the pressure of gas inside the closed pores that tends to expand the pores thereafter reaching the minimum total porosity therefore, the linear shrinkage decreases and total porosity rises.

A part of the quartz found in raw materials dissolves in the liquid phase and new crystalline phases such as mullite are formed [8]. Due to transformations occurring during sintering, the liquid phase continuously changes its composition and consequently its viscosity also changes [9]. The final product consists of rather few mullite crystals and undissolved quartz particles embedded in a glassy matrix [10, 11].

The aim of the present investigation was to study the

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influence of sintering conditions on the reliability of ceramic Raschig rings. The approach was an analysis of the scatter of experimental data, obtained using compressive strength testing, carried out on suitable specimens that were shaped by process extrusion and sintered at different soaking temperatures and for different times. The statistical analyses were also compared with microstructural observations.

Materials and methods

Industrial processed kaolin was used in this study and its chemical analysis is reported in Table 1. The mineralogical analyses of the starting material and fired specimens were carried out using X-ray diffraction (Philips, PW 1130/90). The main constituents of the raw material are kaolinite, illite and quartz. The ceramic Raschig rings were prepared by extrusion of a paste that contained 30 wt% water/dry solid, using a laboratory extruder. The extruded specimens were dried at 110°C and sintered in an electrical laboratory kiln using two different maximum firing temperatures, 1200 and 1250°C with several soaking times ranging from 30 to 180 minutes. For all of the sintered specimens linear shrinkage, water absorption, bulk density, true density and open porosity were measured according to standard methods [12, 13]. The total porosity was calculated as follows and the difference between total and open porosity gives the value of closed porosity:

$$total\ porosity = 1 - \frac{bulk\ density}{ture\ density} \quad (1)$$

The value of the diametric compressive strength was obtained by a standard machine for at least 20 samples in each case (Adamel Lhomargy DY-26, France). Weibull statistical analysis was carried out on each set of strength data using the following equation [14-16]:

$$P_n = 1 - exp\left[-\left(\frac{\sigma-\sigma_t}{\sigma_o}\right)^m\right] \quad (2)$$

where P_n is the probability of failure, σ is the fracture stress, σ_t is the threshold stress below which the probability of failure is zero, σ_o is a normalizing parameter often selected as a characteristic stress at which the probability of failure is 0.632 and m is the Weibull modulus which describes the narrowness of the distribution. The value of σ_t is zero for brittle materials such as ceramics. Several probability functions were used to estimate the fracture stress. Among them the following equation was selected [16]:

$$P_i = \frac{i}{N+1} \quad (3)$$

where N is the number of the measurements and i is the ranking number, where i = 1 is for the weakest specimen and i = N is for the strongest of them. The Weibull modulus m and the parameter σ_o were determined by rearranging equation (2) as:

$$ln\ ln\left(\frac{1}{1-P_i}\right) = m\ \ln(\sigma-\sigma_t) - m\ \ln\sigma_o \quad (4)$$

The scattering in the compressive strength data was evaluated on the base of the variance analysis. The results make a better understanding of the microstructural role in determining the mechanical behavior of specimens under a compressive stress. To clarify this dependence, extensive observation of the microstructures of fractured surfaces of Raschig rings were performed using scanning electron microscopy (SEM, model EOL 4401).

Table 1. the chemical and mineralogical analysis of raw material

mineralogical analysis	chemical analysis	
minerals	weight %	oxides
kaolonite	58 ± 1	SiO_2
illite	28 ± 1	Al_2O_3
quartz	0.35	Fe_2O_3
others	<0.25	TiO_2
	<0.50	CaO
	<0.15	MgO
	4.50	K_2O
	<0.20	Na_2O
	Trace	SO_3
	6.0	L.O.I

Results and discussion

The values of shrinkage and water absorption versus soaking time at 1200 and 1250°C are presented in Figure 1. By increasing the soaking time, the linear shrinkage increases to a maximum value, while the water absorption decreases. When the sintering temperature decreases, a longer soaking time is necessary to obtain zero water absorption.

The open, total and closed porosity values of specimens fired at 1200 and 1250°C during different soaking times are reported in Table 2. As the soaking time increases both the open and total porosity decrease while the closed porosity increases, practically reaching a point where all the pores are closed. The soaking time required to obtain the lowest values of total porosity increases as the maximum sintering temperature decreases.

The XRD analysis shows the presence of quartz and mullite crystals (Figure 2). By increasing the soaking time, the quartz peak intensity decreases. This means, if the soaking time is sufficient to reach zero water absorption even when the sintering temperatures are different, a similar mineralogical composition can be obtained in the sintered specimens. Also, increasing the sintering temperature leads to a more consistent development of the glassy phase.

The average value of the diametric compressive strength at different soaking temperatures and times are shown in Table 3. It is obvious that the maximum strength was

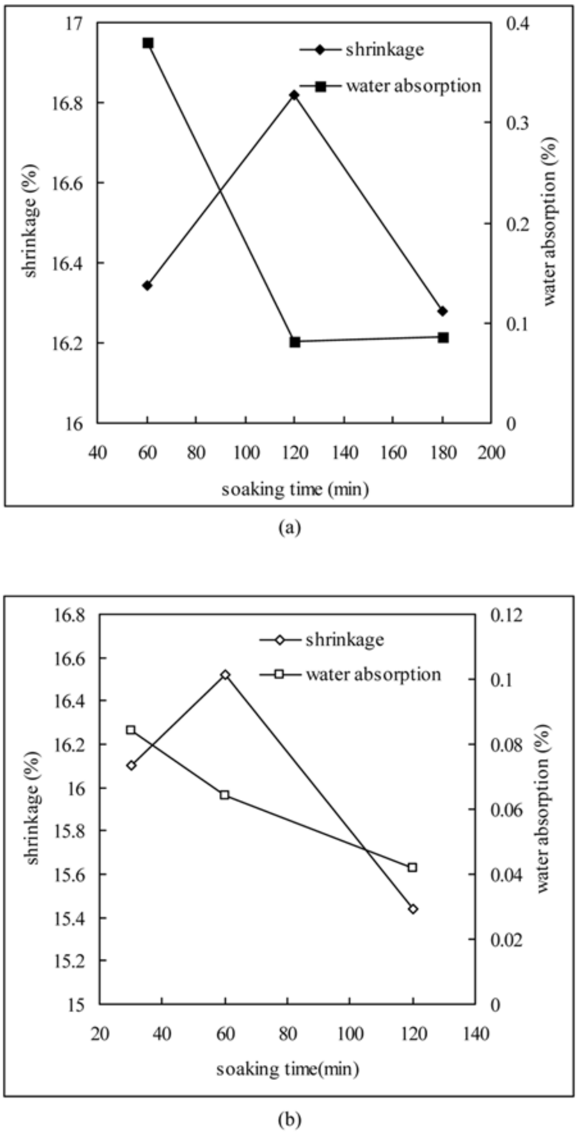


Fig. 1. the values of shrinkage and water absorption versus soaking time at (a)1200°C and (b) 1250°C.

obtained when the total porosity reached the minimum value for each temperature with a little decrease found at 1250ºC and optimum soaking time (60 minutes). It should be emphasized that a soaking time greater than 60 minutes shows no further significant increase in mechanical strength of Raschig rings at 1250°C.

For the statistical analysis of compressive strength, the values of lnln(1/1-P_n) were plotted versus inσ according

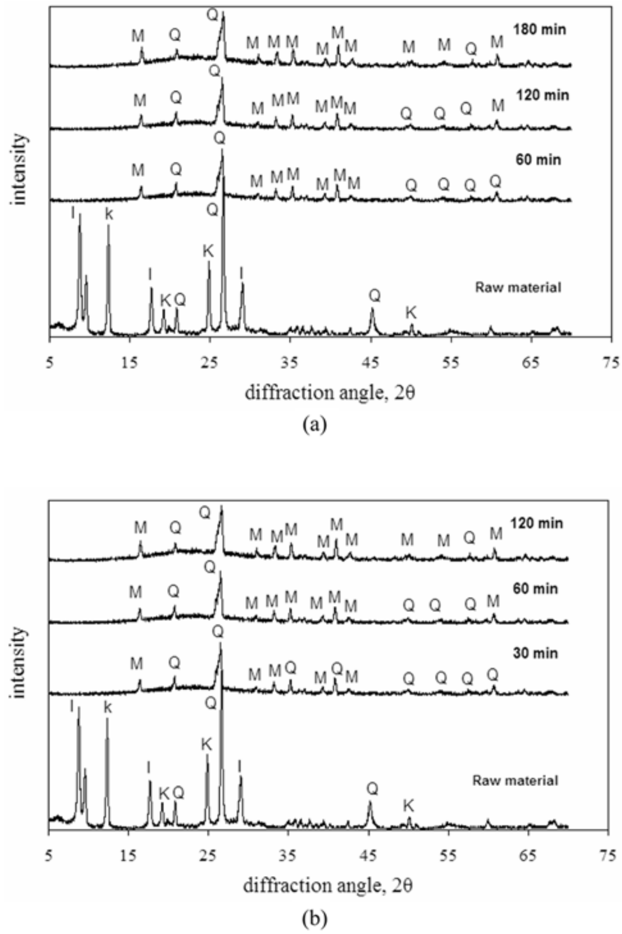


Fig. 2. XRD pattern of specimens sintered at (a) 1200 and (b) 1250°C during different soaking times (K: kaolinite, I: illite, Q: quartz, M: mullite).

to equation (4). The plots show the satisfactory fits of the proposed probability equation (Figure 3). Also, the linear correlation coefficients, R, and Weibull parameters are summarized in Table 3. It can be observed that the reliability of ceramic Raschig rings reach a maximum value as the soaking time increases. The data of Table 3 show that the maximum Weibull modulus is obtained when the total porosity in the ceramic body reaches a minimum value at each temperature. It is observed that the maximum reliability of ceramic Raschig rings is achieved when they are sintered at a lower temperature and for a longer optimum soaking time.

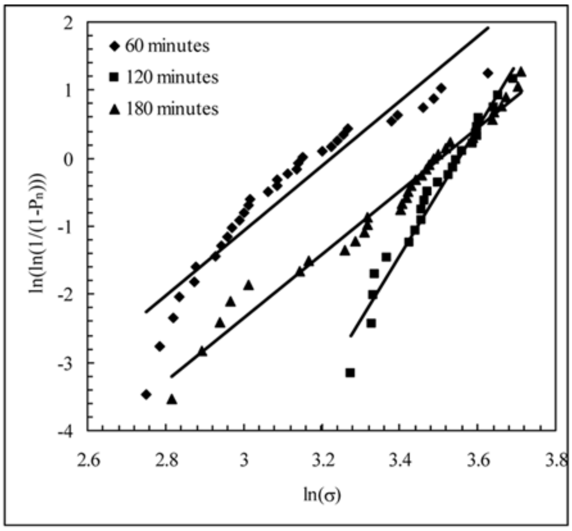
The fracture surfaces of specimens sintered at

Table 2. the values of open, total and closed porosity at 1200 and 1250°C at different soaking times

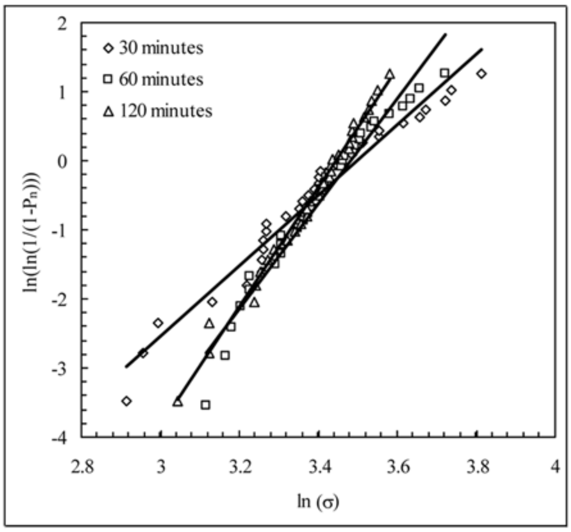
temperature (°C)	soaking time (minutes)	open porosity (%)	total porosity (%)	closed porosity (%)
1200	60	0.95	6.95	6
	120	0.65	6.8	6.15
	180	0.20	7.56	7.36
1250	30	0.30	6.42	6.12
	60	0.20	6.56	6.37
	120	0.34	7.93	7.59

Table 3. parameters of Weibull equation and average compressive strength

temperature (^oC)	soaking time (minutes)	m	σ_0	R	average strength (MPa)
1200	60	3.75	24.715	0.97	22.30 ± 2.60
	120	9.44	34.35	0.98	32.35 ± 2.11
	180	4.65	33.24	0.97	30.41 ± 2.89
1250	30	5.09	31.67	0.96	29.83 ± 3.40
	60	7.58	32.51	0.98	30.60 ± 2.71
	120	8.64	31.35	0.97	29.30 ± 2.64



(a)



(b)

Fig. 3. Weibull plots for the specimens sintered at (a) 1200 and (b) 1250^{o}C and different soaking times.

1250^{o}C and 30 minutes shows a microstructure with low homogeneity, characterized by some closed round pores (Figure 4a). A longer soaking time fosters the development of a large amount of glassy phase, so the interconnected porosity tends to disappear in agreement with the minimum porosity results, reported in Table 2. As shown in Figures 4b and 4c, at the optimum sintering conditions ceramic Raschig rings were able to reach a minimum porosity, the pores are generally spherical and they are larger when sintered at 1250^{o}C for 60 minutes. It is interesting to note that too large an increase in the soaking time causes abnormal growth of closed pores which results in a decrease in mechanical strength and reliability of rings consequently (Figure 4(d)). Also, an increase in mullite content as shown in Figure 2 can improve the reliability of ceramic Raschig rings.

Conclusions

The sintering behaviour of a ceramic Raschig ring composition was studied at 1200 and 1250^{o}C using different soaking times ranging from 3 to 180 minutes. Based on the experimental investigations reported in this study, the conclusions can be summarized as follows: Weibull analysis is a powerful tool to increases knowledge about the reliability of ceramic Raschig rings providing a reliable method to understand the effects of compressive stress on the lifetime of ceramic Raschig rings. During the sintering process, the development of the liquid phase progressively causes a decrease in both open and total porosity until a minimum value is reached while the closed porosity increases. At lower maximum sintering temperature to reach a minimum value of the total porosity with a longer soaking time becomes necessary. Furthermore, the value of total porosity is independent of sintering temperature at the optimum soaking time. By increasing the soaking time, the Weibull modulus increases up to a maximum value which is subsequently reduced due to gas pressure inside closed pores. This phenomenon causes a meaningful growth of the pore size and a low homogeneity of microstructure. The microstructural analysis shows that the pore size of the specimens characterized by zero water absorption is considerably influenced by the soaking temperature and time. Therefore a minimum porosity as well as a maximum reliability of ceramic Raschig rings can be obtained by sintering at a lower temperature with an optimum soaking time.

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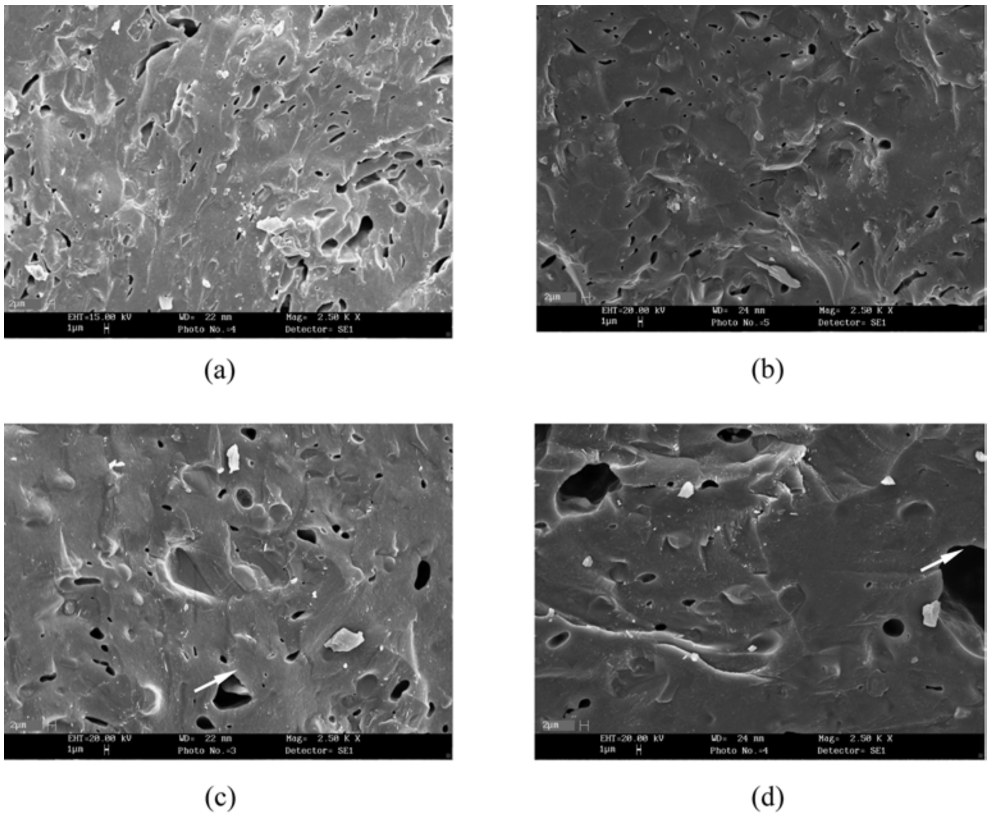

Fig. 4. the SEM micrograph of specimens sintered at (a) 1250°C and 30 minutes, (b) 1200°C and optimum soaking time, 120 minutes, (c) 1250°C and optimum soaking time, 60 minutes, (d) 1250°C and 120 minutes.

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