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Statistical Optimization of the Binder Mixing Ratio for Fabricating Reliable Ceramic Raschig Rings

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Abstract

Several types of ceramic Raschig rings have been developed for extreme chemical and waste treatment processes. The compressive strength and reliability of ceramic Raschig rings are basically affected by the mixing ratio of the materials used and the quality control of the shaping process. To optimize the above-mentioned properties, various experiments have been conducted. In the present investigation polyvinyl alcohol, carboxymethyl cellulose and Arabic gum were selected and used in an experimental design algorithm. Different amounts of binders were added to a typical kaolin under conditions similar to those found in industrial practice. Different combinations of clay and binders were prepared according to the mixture design algorithm and shaped with the extrusion technique. The test rings were sintered at 1270 °C and characterized by determining their linear shrinkage, water absorption, porosity and compressive strength. The strength data were statistically analyzed based on the Weibull theory to mathematically describe the reliability of the rings. Regression models were calculated for correlating the above properties in order to optimize the binder mixing ratio. The suitable amounts of binders were reported and the variation in the Weibull modulus was confirmed by means of scanning electron microscopy.

Keywords: Raschig ring, extrusion, compressive strength, reliability.

I. Introduction

The most commonly used material in the production of ceramic beds is kaolin containing a relatively high proportion of illite, kaolinite and quartz, and a lower proportion of impurities. This type of ceramic was fabricated for many years. This group of ceramics should demonstrate high technical performance during application [1]. A decrease in the number and size of defects in the structure of ceramic beds during shaping and heating processes improves theire technical characteristics [2].

Recently, the reinforcement of ceramic packed beds was considered in the chemical and oil industries. Ceramic Raschig rings provide the contact surface for gas and liquid phases especially in acidic environments, for example waste-water treatment [3]. The reinforcement of the rings is needed because these materials are widely preferred for use in randomly packed beds owing to their capability of withstanding aggressive environments and the possibility of their fabrication with sufficient strength. Ceramic Raschig rings are manufactured in a cylindrical shape with equal dimensions in external diameter and height.

Different mechanisms were proposed for the reinforcement of the ceramic bodies. The reinforcement of ceramic beds can be achieved with two methods as previously reported by other researchers: (i) Matrix reinforcement based on the addition of dispersive particles such as alumina and zirconium silicate [4]; (ii) Improvement of defects and pore morphology to obtain a body with a homogenous microstructure [5]. In the first method, alumina and zirconium components are often used to improve mechanical behavior [4]. The substitution of part of the kaolin with alumina or zirconium silicate decreases the abrupt change in thermal expansion owing to $\alpha \rightarrow \beta$ inversion of quartz [6]. Shirchi *et al.* reported that the use of 10 wt% alumina or 5 wt% zirconium silicate in the composition of ceramic Raschig rings substantially improves their compressive strength and reliability [7]. A pronounced improvement in reliability is observed in bodies that contain fine particles of alumina in the size range 1 – 2 μm [6].

The influence of defects and pores on the mechanical properties of ceramic Raschig rings has been reported by many researchers. Villora *et al.* studied the effect of the shaping process on the mechanical strength and reliability of Raschig rings [8]. They concluded that the extrusion process is the most suitable green forming method with regard to strength and reliability compared to slip casting and uniaxial pressing methods. The results of recent investigations conducted out by Salehi and Salem showed that the suitable moisture content for fabricating reliable rings ranges between 20 and 25 wt% as this minimizes porosity. The defects with small dimensions produced in the microstructure of the rings is the another reason for shaping the rings with minimum moisture content in the ceramic body [9].

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Several groups have investigated the effect of fluxing agents on the sintering and mechanical behavior of finished ceramic products [10, 11]. The results reported by Esposito *et al.* indicated that the presence of 5 wt% nepheline syenite in porcelain stoneware body compositions significantly decreases the total porosity up to 2.5 % and considerably improves the bending strength as well as the Weibull modulus [5]. The study conducted by Rostami and Salem also showed that the addition of 5 wt% nepheline syenite to the composition of ceramic Raschig rings is sufficient to minimize the total porosity and improve both compressive strength and reliability at the same time [12].

Ceramic products manufactured from red clay contain large defects in their body structure. Lee *et al.* studied the mechanical behavior of ceramic bodies prepared with different red clay-binder combinations [13]. They reported that the body strength depends heavily on the type and amount of binder used in the starting formulation. The mechanical characteristics of specimens prepared with polyvinyl alcohol and carboxymethyl cellulose were comparable with those for bodies shaped without binders [14].

The mixture design method and response surface analysis, which have been used in many studies, are based on statistic and mathematical methods for optimizing compositions by improving their properties. Many combinations of materials are formulated by mixing components; the quality of the final product depend on the combination ratio of the starting materials. The mixture design method has been demonstrated to optimize material properties such as the viscosity of slips [15], shrinkage, water absorption [16] and waste substances used in body composition [17]. The synergetic effect of two or three components on material characteristics can be easily identified with the mixture design method. With this empirical approach, the total amount of materials is considered to be constant and a measured property of the mixed composition is evaluated as a function of the component fractions. The main purpose of this method is therefore to determine the optimum composition in which the required property is achieved. The best composition can be determined by using the composition-property in a triaxial diagram. In addition to quantitative evaluation, a polynomial equation that defines the property as a function of the combination ratio can be correlated. Therefore, the quantitative estimation of the given property is obtainable in the studied system without the need for a large number of experimental data [18].

In a system with n components, there are $n-1$ independent compositions, x_i. The polynomial function, F, can be expressed in following form:

$$F = \sum_{i=1} \beta_i x_i + \sum_{i<j}\sum \beta_{ij} x_i x_j + \sum_{i<j}\sum \beta_{ij} x_i x_j (x_i - x_j) + \sum_{i<j}\sum_{j<k}\sum \beta_{ijk} x_i x_j x_k \tag{1}$$

where β is the constant of the equation. This equation should be evaluated over q number of points. Therefore, a laboratory study consisting of $q>n$ experiments must be conducted and the value of property on the selected lattice points should be evaluated. The correlation presented as Eq. 1 is fitted to experimental data and the validity of the model is acceptable if the differences between the experimental data and computational values are close to zero with acceptable variance.

The control of defect dimensions and pore morphology in the structure of ceramic Raschig rings can offer many possibilities to improve the performance of packed beds. For example, the compressive strength and reliability of rings can be improved with the addition of binders to the starting composition owing to the significant decrease in the defect size. Industrial experience has demonstrated that the combination of binders, especially the mixture of polyvinyl alcohol, carboxymethyl cellulose, and Arabic gum, affects the properties of the final products. The effect is determined by the trial and error method on industrial scale. In the present study the statistical mixture design method was applied to obtain the best combination of the above-mentioned binders to add to typical kaolin as a starting raw material. Also, the reliability of rings has been carefully evaluated based on the Weibull theory.

II. Materials and Methods

Industrial kaolin powder was used as a starting material in the present study. The chemical composition of clay determined with the XRF technique (Model S4 Explorer 7KP103, Brucker, Karlsruhe, Germany) shows that the raw material contains SiO_2: 58.00, Al_2O_3: 28.00, K_2O: 4.50, Na_2O: 0.20, CaO: 0.50, MgO: 0.15, Fe_2O_3: 0.35, TiO_2: 0.25 and L.o.I.: 6.00 wt% (loss on ignition). Mineralogical analysis of the used kaolin determined with X-ray diffraction (Model D5000 Siemens, Germany) indicated kaolinite, illite, pyrophillite and quartz as the main minerals. The binders used were polyvinyl alcohol, carboxymethyl cellulose, Arabic gum, which are denoted by PVA, CMC and AG respectively. The ternary binder systems, Fig. 1, were mixed with de-ionized water in an agitator for 2 h. The maximum amount of PVA and CMC was 1 wt% and the maximum amount of AG is 1.75 wt% owing to its solubility in water. The solutions were added to the clay powder and mixed for 4 h, and then the pastes were left for 48 h to obtain homogeneous materials before being de-aired in a laboratory pug mill to prepare the bodies for extrusion. The bodies were fed into a laboratory single-screw extruder, a prototype, to shape the ceramic Raschig rings at a rate of 60 cm/min. Approximately 2 wt% of body moisture was removed during the extrusion process. The specimens were dried at 100 °C for 24 h. The dry specimens were heated (Model EX. 1500 – 6L, Iran) at rate of 5 °C/min up to 573 °C and kept at this temperature for 1 h. After the organic materials had been removed and $\alpha \rightarrow \beta$ inversion of quartz had taken place, the specimens were then heated from 573 to 1270 °C at a heating rate of 10 °C/min. The specimens were sintered at 1270 °C and then naturally cooled to reach room temperature.

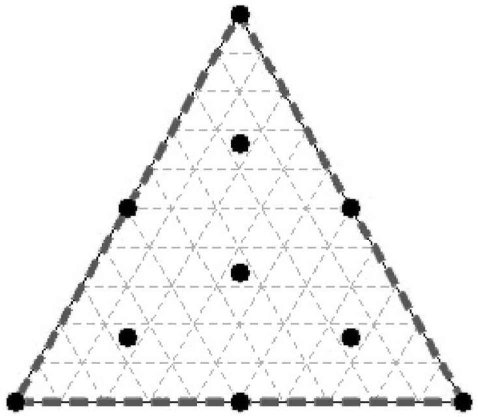

Fig. 1: The compositions of ceramic Raschig rings prepared according to the mixture design method.

Phase identification was performed with the XRD method (Model D5000 Siemens, Germany). The XRD pattern shows the presence of residual quartz and newly formed mullite crystals embedded in glass phase. The linear shrinkage, bulk density, open and closed porosity of dry and fired specimens were measured according to the standard procedures [19, 20]. The compressive strength of dry and fired specimens was determined with a universal test machine (Model Adamel Lhomargy DY-26, France). According to the findings of a previous study conducted by Salehi and Salem, the reliability of rings can be described with the Weibull statistical method as the following correlation [21]:

$$P_i = 1 - \exp\left[-\left(\frac{\sigma_i}{\sigma_0}\right)^m\right] \quad (2)$$

where P_n is the probability of failure at stress of σ_i, σ_0 is the characteristic strength and m is the Weibull modulus indicating the scatter of the strength data. The probability of failure was calculated according to $P_i=i/N+1$, which has been reported as a suitable function for computing this parameter [21]. In this equation i is the ranking number and N is the total number of specimens used in the mechanical tests for each run. At least twenty specimens were used in the evaluation of the reliability of each composition.

The fracture surfaces of specimens were observed with a scanning electron microscope (Model EOL-4401, England) to analyze the effect of defects and pores on the mechanical properties. For this purpose, the samples were placed on copper supports using a polymer and coated with gold in a vacuum system.

III. Results and Discussion

The physical properties of the dry rings prepared with different amounts of binders are detailed in Table 1. The bulk density of the dry specimens containing binders is comparable with that of body prepared from kaolin only, STD. It increases up to 1.68 g/cm^3 when 0.5 % CMC and 0.88 % AG are added to the starting material. The addition of the above-mentioned amounts of binders to the composition of the rings causes an appreciable decrease in the total porosity of the dry specimens and affects the porosity probably based on the coherence between the surfaces of the clay particles. The sharp increase in bulk density and significant decrease in porosity are related to the greater compaction of the body during extrusion compared to the reference body, STD. The bulk density as well as the porosity of the dry specimens exhibit significant variation with the addition of binders except in the case of the maximum content of CMC, which shows an inflexion in density. The formation of defects in the structure of the ring is probably responsible for the behavior observed.

Table 1: Physico-mechanical properties of dry rings containing different amounts of binders.

PVA (%)	CMC (%)	AG (%)	Bulk density (g/cm^3)	Total porosity (%)	Dry body strength (kPa)
0.00	0.00	0.00	1.56±0.01	32.00±0.40	28±1
1.00	0.00	0.00	1.64±0.01	28.66±0.40	383±4
0.00	1.00	0.00	1.60±0.01	30.25±0.40	163±4
0.00	0.00	1.75	1.69±002	26.45±0.80	139±3
0.50	0.50	0.00	1.66±0.01	28.03±0.40	253±2
0.17	0.17	1.17	1.64±0.02	28.76±0.80	182±1
0.17	0.66	0.29	1.63±0.01	28.94±0.40	193±2
0.66	0.17	0.29	1.65±0.02	28.44±0.80	305±4
0.00	0.50	0.88	1.68±0.01	27.05±0.40	195±3
0.50	0.00	0.88	1.65±0.01	28.26±0.40	255±4
0.34	0.34	0.58	1.65±0.01	28.44±0.40	192±2

Dry compressive strength rises with the increment in amounts of binders compared to that for the STD ring. The strength was also found to decrease with addition of AG to the composition, indicating the weak coherence between the particles. A sufficient increment in strength is observed in rings containing PVA, in which the maximum value was achieved with the addition of 1 wt% of this binder. Based on the measured values for dry strength, Table 1, the following equation can be presented for dry strength as a function of the binder fractions with the help of Minitab software (Parnian, Version 15, Iran). This model was statistically found to be most adequate with a regression coefficient of $R^2 = 99.3$ %:

$$\sigma_D = 384.3x_1 + 164.3x_2 + 140.3x_3 - 74.9x_1x_2 - 18.9x_1x_3 + 181.1x_2x_3 - 966.7x_1x_2x_3 + 90.0x_1x_2(x_1 - x_2) + 156.0x_1x_3(x_1 - x_3) \quad (3)$$

where σ_D is the dry strength, x_1 is the PVA fraction, x_2 is the CMC fraction and x_3 is the AG fraction divided by 1.75. In addition, the corresponding response surface is shown in Fig. 2. The response surface plot is a graphical presentation of Eq. 3 and allows rapid prediction for the entire compositions under investigation. This figure indicates that the dry strength increases with the PVA content and it reaches a maximum value in the presence of 1 wt% PVA. However, the ring prepared with maximum amount of AG, 1.75 wt%, exhibits low dry strength. Fig. 2 also indicates that the mixing of CMC and AG negligibly affects dry strength and PVA is a suitable binder with the best performance for improving strength after drying.

The physical properties of sintered ceramic Raschig rings, listed in Table 2, indicate that the combination of binders cannot influence linear shrinkage with the exception of the addition of 1 % PVA which caused a sharp increase in shrinkage. With selection of an appropriate combination of binders it is possible to control the linear shrinkage close to that for STD ring.

The water absorption of the STD composition is very low, which is the result of the sintering of rings at high temperature. The variation of data is not similar to the shrinkage behavior. It is evident that some of the open pores were negatively formed in final products. The lowest water absorption is observed in the ring prepared with 0.17 % PVA, 0.66 % CMC and 0.29 % AG. A sharp increase in the water absorption of the ring prepared with the addition of 0.17 % PVA, 0.17 % CMC and 1.17 % AG may be the result of the formation of defects with large dimensions that absorb the high content of water. The low value of water absorption in the ring prepared with the addition of just 1 % CMC or 1.75 % AG may be due to the formation of closed pores in the sintered rings.

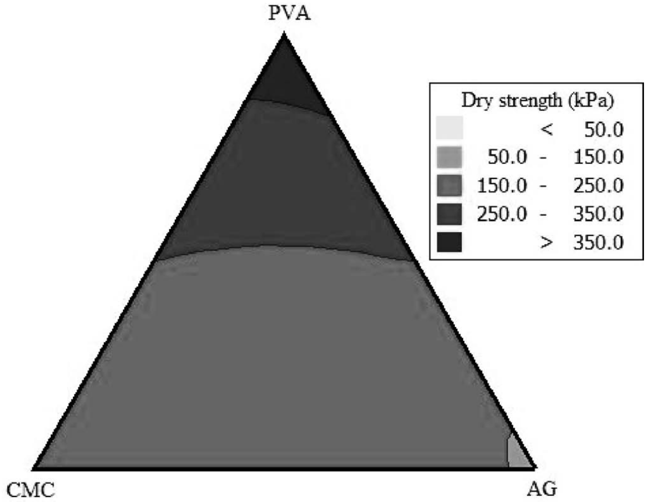

Fig. 2: Variation of dry compressive strength as a function of the ring composition according to the mixture design method.

The bulk densities of the sintered specimens remain approximately constant with the addition of binders with the exception of the addition of 1 % PVA. This phenomenon clearly indicates that total porosity remains constant near to that for the STD ring. The porosity of specimens reported in Table 2 shows that most pores are closed in all compositions studied.

Table 2: Physical properties of sintered rings containing different amounts of binders.

PVA (%)	CMC (%)	AG (%)	Shrinkage (%)	Water absorption (%)	Bulk density (g/cm^3)	Total porosity (%)	Closed porosity (%)
0.00	0.00	0.00	15.0±0.2	0.26±0.00	2.36±0.01	6.6±0.4	5.8±0.2
1.00	0.00	0.00	15.8±0.3	0.43±0.03	2.43±0.02	3.8±0.8	3.3±0.7
0.00	1.00	0.00	15.3±0.1	0.26±0.01	2.37±0.01	6.5±0.4	5.9±0.2
0.00	0.00	1.75	16.2±0.2	0.29±0.01	2.41±0.01	4.7±0.4	4.1±0.3
0.50	0.50	0.00	15.3±0.2	0.93±0.01	2.38±0.01	5.7±0.4	3.5±0.1
0.17	0.17	1.17	15.4±0.2	1.34±0.04	2.36±0.01	6.9±0.4	3.3±0.3
0.17	0.66	0.29	15.1±0.1	0.25±0.01	2.37±0.00	6.1±0.2	5.5±0.1
0.66	0.17	0.29	15.2±0.2	0.35±0.01	2.38±0.00	5.8±0.2	4.9±0.1
0.00	0.50	0.88	15.3±0.2	0.48±0.01	2.38±0.00	6.0±0.2	4.8±0.1
0.50	0.00	0.88	15.3±0.2	0.38±0.01	2.38±0.01	5.6±0.4	4.9±0.3
0.34	0.34	0.58	15.3±0.2	0.86±0.01	2.36±0.01	6.6±0.4	4.5±0.4

Table 3: Mechanical properties of sintered rings containing different amounts of binders.

PVA (%)	CMC (%)	AG (%)	Average strength (MPa)	Weibull modulus			Characteristic strength (MPa)		
				m	m_{lower}	m_{upper}	σ_0	σ_{0lower}	σ_{0upper}
0.00	0.00	0.00	20.5±2.6	3.4	2.4	4.2	25.9	23.2	29.0
1.00	0.00	0.00	31.7±4.6	8.2	5.4	10.6	33.7	31.9	35.7
0.00	1.00	0.00	33.5±4.9	8.4	5.6	10.7	35.6	33.8	37.6
0.00	0.00	1.75	36.6±7.3	5.7	3.9	7.1	39.6	36.8	42.4
0.50	0.50	0.00	29.4±4.6	7.3	4.6	9.5	31.3	29.1	33.7
0.17	0.17	1.17	26.5±3.8	7.5	5.4	9.4	28.3	28.9	29.8
0.17	0 .66	0.29	34.9±3.2	10.4	7.1	13.2	36.6	35.3	38.0
0.66	0.17	0.29	29.2±5.0	6.6	4.4	8.5	31.3	29.2	33.6
0.00	0.50	0.88	35.6±3.7	11.2	7.3	14.5	37.3	35.7	39.0
0.50	0.00	0.88	24.2±2.9	10.0	6.7	12.7	25.5	24.4	26.7
0.34	0.34	0.58	28.9±3.3	8.7	6.2	10.8	30.6	29.3	32.0

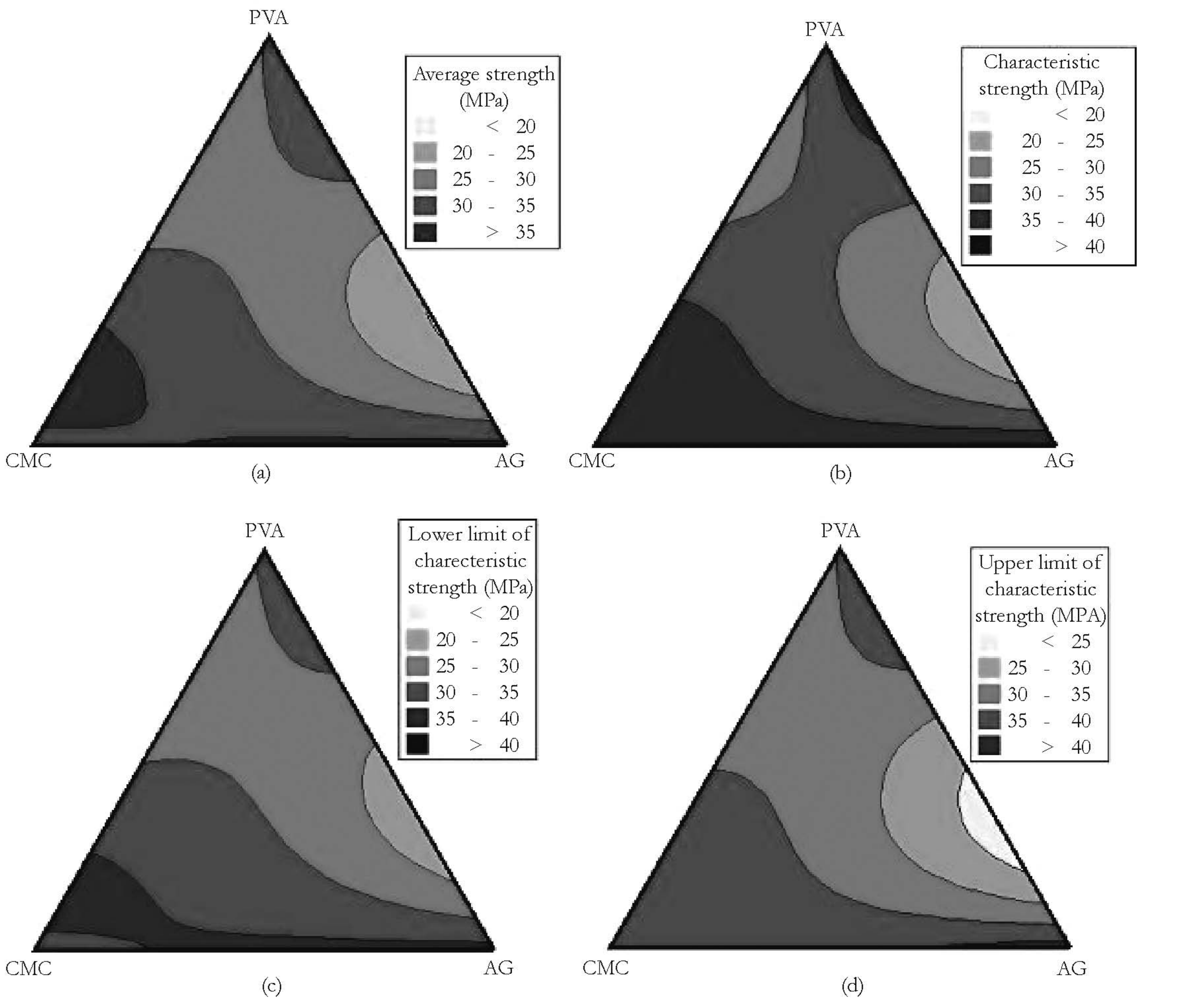

Fig. 3: Variation of (a) average strength, (b) characteristic strength, (c) lower limit of characteristic strength and (d) upper limit of characteristic strength as a function of the ring composition according to the mixture design method.

The mechanical properties of produced rings are reported in Table 3 for the studied compositions. The response surface plot, Fig. 3a, shows that the average strength varies non-linearly with the content of binders and reaches the maximum value with the addition of CMC or AG. On the contrary, the amount of PVA cannot be increased up to 1 % owing to the significant change in shrinkage. For this reason, the PVA content cannot be increased by more than 0.17 %. The following equation correlates the strength of sintered Raschig rings, σ, with the binder fractions:

$$\begin{aligned}\sigma = {} & 31.72x_1 + 33.52x_2 + 36.62x_3 - 12.74x_1x_2 \\ & - 39.74x_1x_3 + 2.26x_2x_3 + 18.21x_1x_2x_3 \\ & - 54.00x_1x_2(x_1 - x_2) + 84.60x_2x_3(x_2 - x_3)\end{aligned} \tag{4}$$

This equation is used to obtain the composition that exhibits the maximum strength. Eq. 4 and the data of Table 3 indicate that the strength is more sensitive to changing amounts of CMC and AG. In contrast, the amount of PVA can be increased up to 0.17 % without resulting in any significant change in shrinkage. Fig. 3 also shows that strength increases significantly as the amount of CMC rises more than 0.5 wt%. It reaches 35 MPa if 0.17 % PVA, 0.66 % CMC and 0.29 % AG are added to the composition. On the other hand, with the use of 1.75 % AG, maximum strength is achieved.

In order to understand the effect of the binder mixing ratio on the reliability of ceramic Raschig rings, the Weibull modulus was determined for the sintered rings prepared with different amounts of binders, Table 4. For this purpose, the system of equations obtained by maximizing the logarithm likelihood function for *N* number of the failed specimens is given by the following equations [22]:

$$\frac{\sum_{i=1}^{N}(\sigma_i)^m \ln(\sigma_i)}{\sum_{i=1}^{N}(\sigma_i)^m} - \frac{1}{N}\sum_{i=1}^{N}\ln(\sigma_i) - \frac{1}{m} = 0 \tag{5}$$

and

$$\sigma_0 = \left[\frac{\sum_{i=1}^{N}(\sigma_i)^m}{N}\right]^{\frac{1}{m}} \tag{6}$$

According to the ASTM C-1239 standard method, confidence bounds can be constructed for the estimated Weibull modulus and characteristic strength [22]. The 90 % confidence bound on characteristic strength is obtained from the 5 and 95 percentile distributions. In Table 3, the lower and upper bounds of the Weibull modulus and characteristic strength are reported for the presence and absence of binders. The confidence bounds of the characteristic strength were influenced by the amount and mixing ratio of the binders. For all the modified compositions, a high value of strength is observed compared to that for the STD composition. The composition prepared with 1.75 wt% AG causes a significant improvement in the strength. Eq. 7 can be used to relate the Weibull modulus with the weight fraction of the binders:

$$\begin{aligned}m = {} & 8.15x_1 + 8.35x_2 + 5.65x_3 - 4.21x_1x_2 \\ & + 11.99x_1x_3 + 16.39x_2x_3 - 49.55x_1x_2x_3 \\ & - 37.40x_1x_2(x_1 - x_2) + 14.8x_1x_2x_3(x_1 - x_3)\end{aligned} \tag{7}$$

Also, the following equations can be used for estimation of the lower and upper limits of the Weibull modulus, m_{lower} and m_{upper}, and the characteristic strength, σ_{0lower} and σ_{0upper}:

$$\begin{aligned}m_{lower} = {} & 5.37x_1 + 5.57x_2 + 3.87x_3 - 3.73x_1x_2 \\ & + 8.07x_1x_3 + 10.07x_2x_3 - 16.84x_1x_2x_3 \\ & - 25.60x_1x_2(x_1 - x_2) + 7.40x_1x_3(x_1 - x_3)\end{aligned} \tag{8}$$

$$\begin{aligned}m_{upper} = {} & 10.54x_1 + 10.64x_2 + 7.04x_3 - 4.83x_1x_2 \\ & + 15.17x_1x_3 + 22.17x_2x_3 - 76.45x_1x_2x_3 \\ & - 46.40x_1x_2(x_1 - x_2) + 19.60x_1x_3(x_1 - x_3)\end{aligned} \tag{9}$$

$$\begin{aligned}\sigma_{0lower} = {} & 31.98x_1 + 33.88x_2 + 36.88x_3 - 14.69x_1x_2 \\ & - 39.49x_1x_3 + 1.91x_2x_3 + 42.14x_1x_2x_3 \\ & - 45.20x_1x_2(x_1 - x_2) + 59.80x_2x_3(x_2 - x_3)\end{aligned} \tag{10}$$

$$\begin{aligned}\sigma_{0upper} = {} & 35.73x_1 + 37.63x_2 + 42.43x_3 - 11.68x_1x_2 \\ & - 49.28x_1x_3 + 3.88x_2x_3 + 23.51x_1x_2x_3 \\ & - 42.80x_1x_2(x_1 - x_2) + 91.60x_2x_3(x_2 - x_3)\end{aligned} \tag{11}$$

The regression coefficients of the equations, R^2, for the prediction of the mechanical behavior were between 98.0 and 99.9. The R^2 values indicate that the presented models can be confidently used to estimate the effect of binders on the above-mentioned properties.

The improvement in the Weibull modulus is most pronounced if the amount of CMC is higher than 0.5 wt%. It is clearly observed that the addition of AG cannot substantially improve the Weibull modulus. Fig. 4 also shows that the increase in the AG content contributes to a decrease in the Weibull modulus, causing a sharp drop in reliability. According to Figs. 3 and 4, there is a suitable range in which the strength and reliability are simultaneously improved by mixing of the binders. The amount of CMC, above 0.66 wt%, contributes to both an increase in strength and the Weibull modulus at the same time. Based on the interaction of Figs. 2 – 4, the common area was selected to maximize the Weibull modulus and strength combined with acceptable dry strength (more than 200 kPa). Hence, based on this approach the optimum combination of binders can be obtained from interactions of dry strength, sintered strength and Weibull modulus in the response surface diagram as presented in Fig. 5. This figure highlights the areas in which the dry strength is higher than 200 kPa, and the average and characteristic strengths are higher than 30 and 32 MPa respectively. In addition, the Weibull modulus is more than 7. Moreover, the lower and upper values of the Weibull modulus were limited by 5 and 10. To fabricate the rings with reliable strength, the confidence bounds of characteristic strength were considered at 30 and 34 MPa respectively.

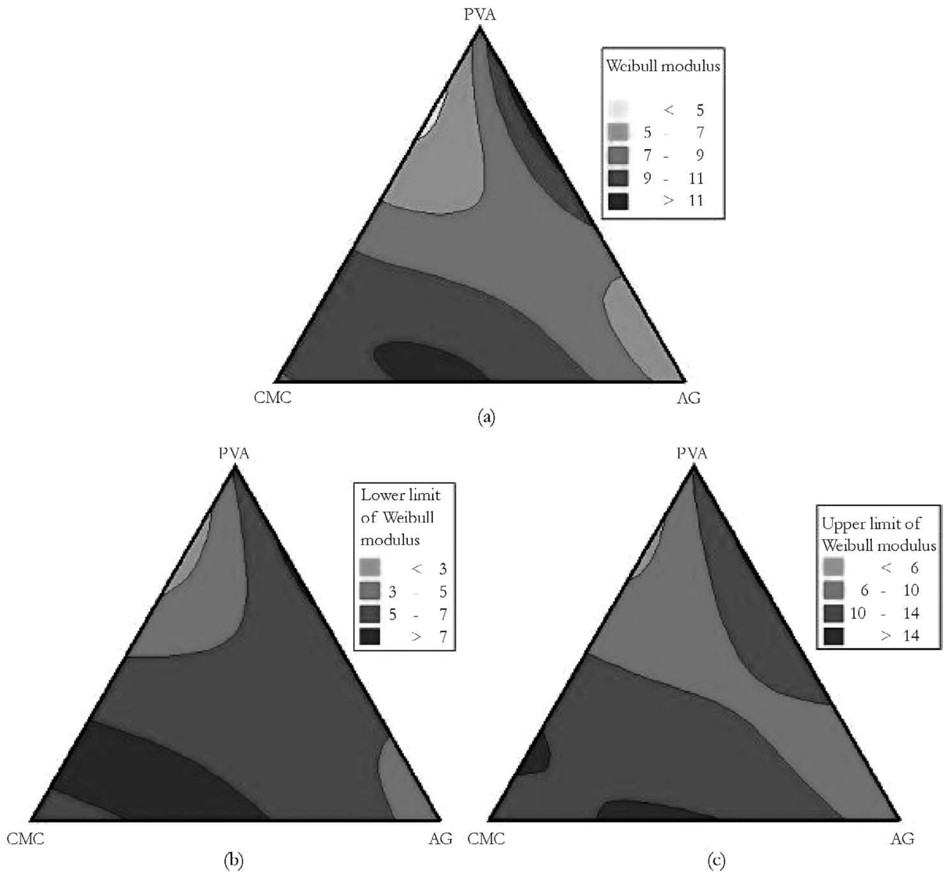

Fig. 4: Variation of (a) the Weibull modulus, (b) lower and (c) upper limits of the Weibull modulus as a function of the ring composition according to the mixture design method.

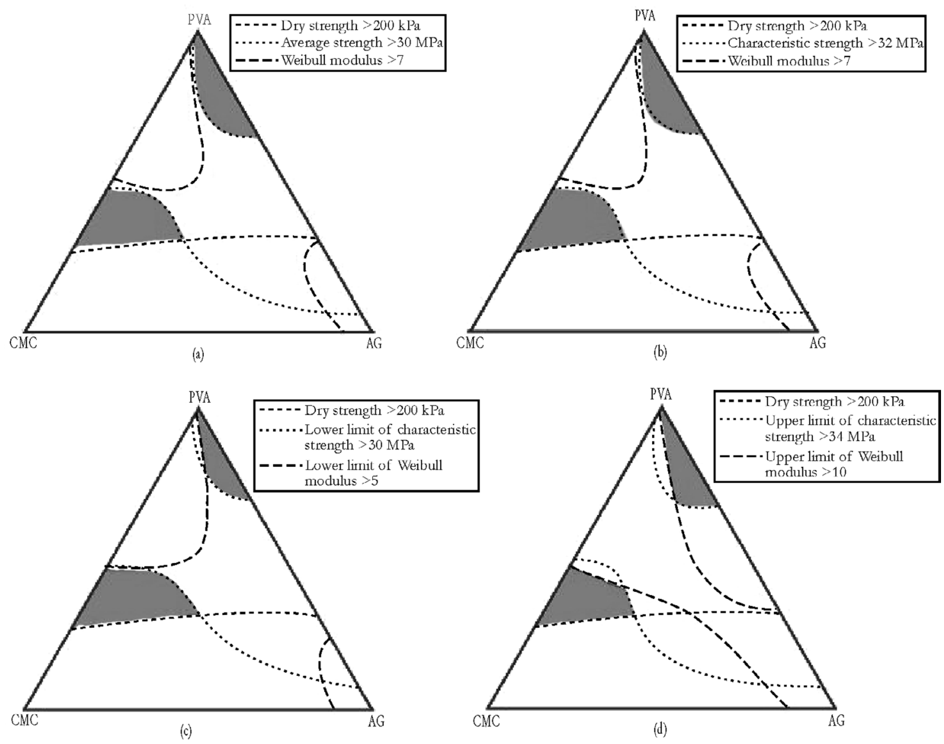

Fig. 5: The interaction of (a) dry strength, average strength and the Weibull modulus, (b) dry strength, characteristic strength and the Weibull modulus, (c) dry strength, lower bound of characteristic strength and lower limit of the Weibull modulus, (d) dry strength, upper bound of characteristic strength and upper limit of the Weibull modulus for determination of suitable binder ranges.

The SEM micrographs of the fracture surface of the specimens prepared with different binder mixing ratio are shown in Fig. 6. In all the SEM photographs elongated defects are observed that affect the mechanical properties of the rings. The number of defects decreased considerably with the addition of PVA and AG. The heterogeneous distribution of defects is the major reason for the reduction in the Weibull modulus of the rings prepared with AG only. A decrease in the number of defects improves strength but their random distribution affects the Weibull modulus as well as the reliability of the rings. The uniform distribution of defects in the body prepared with 0.17 % PVA, 0.66 % CMC and 0.29 % AG causes an appreciable improvement in the Weibull modulus. The small defects are also observed in the SEM photographs. This variation in dimensions was found to increase the compressive strength.

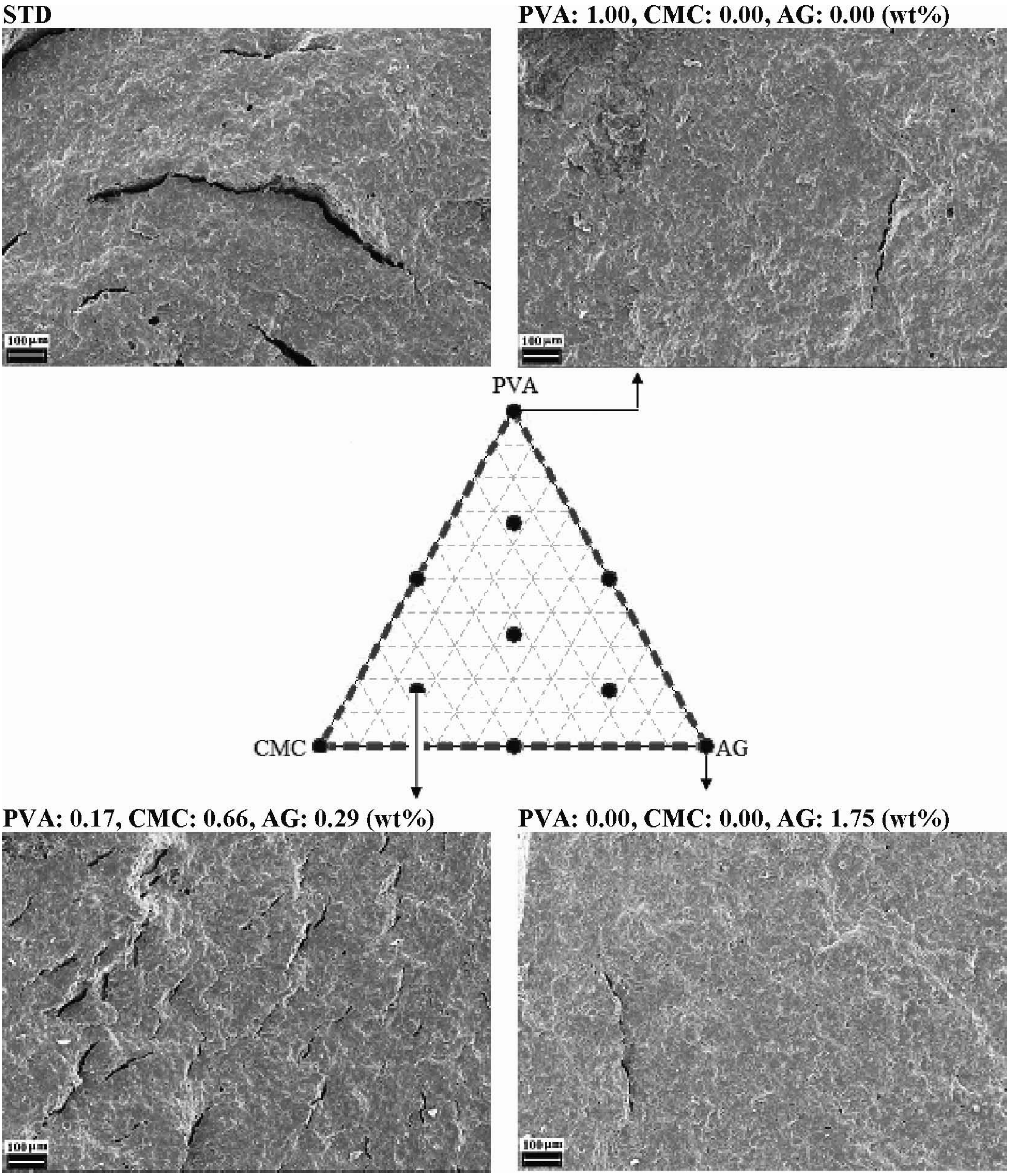

Fig. 6: The defects of rings prepared with PVA, CMC and AG according to the mixture design algorithm.

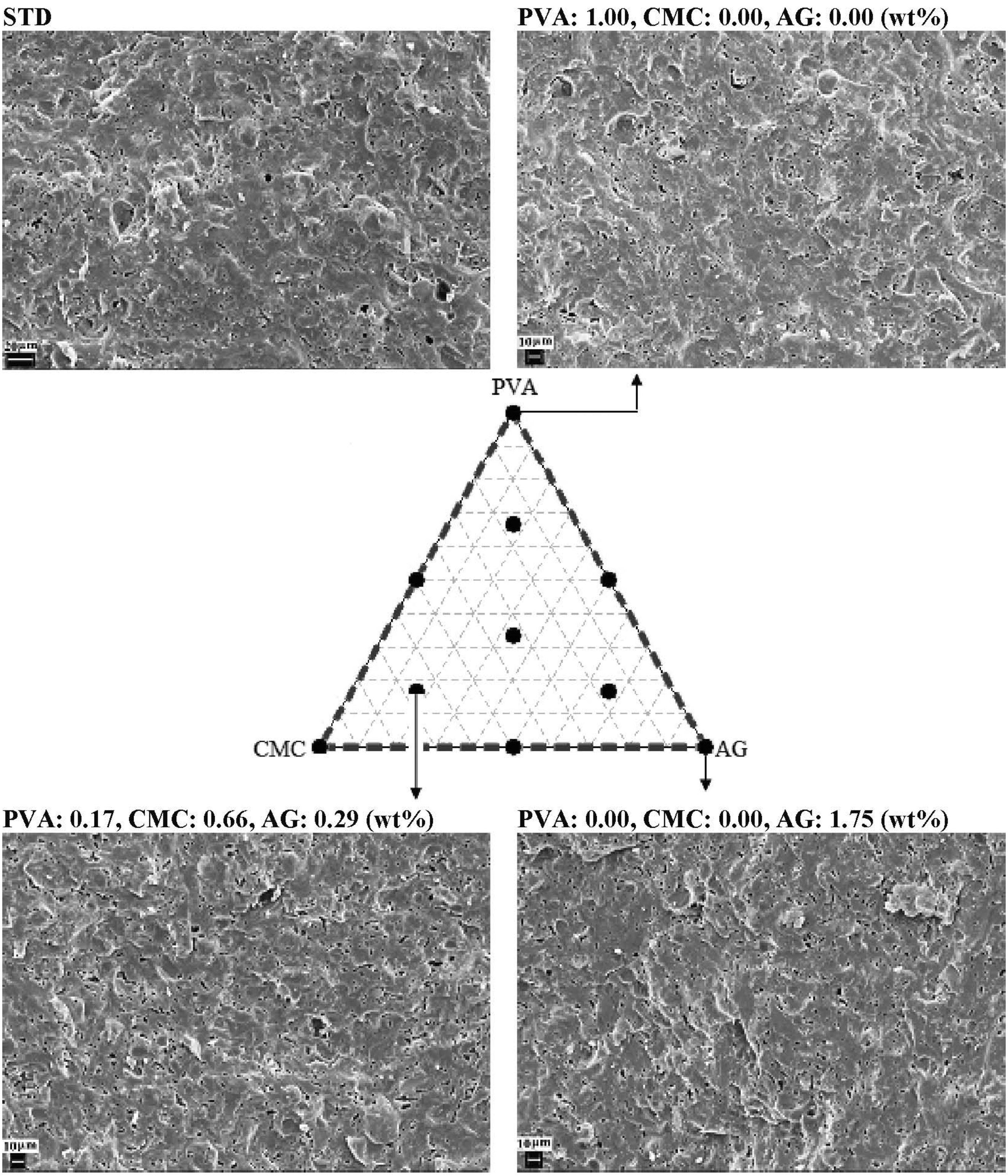

Fig. 7: SEM micrographs of rings prepared with PVA, CMC and AG according to the mixture design algorithm.

The morphology of pores in the rings sintered at 1270 °C is shown in Fig. 7. The spherical shape of the pores detected is the result of the sealing of the pores and the formation of liquid phase at 1270 °C [3]. At this temperature, most of the pores are closed owing to the diffusion of liquid phase into the pores. The microstructure of ceramic bodies is affected by the surface tension/viscosity ratio of liquid phase formed at high temperature. In this investigation the same firing schedule was applied for densification of extruded rings, therefore the micrographs do not indicate substantial differences in the microstructure. It should be noted that the size and distribution of defects are the major factors controlling the strength and Weibull modulus.

IV. Conclusions

The mixture of polyvinyl alcohol, carboxymethyl cellulose and Arabic gum positively promotes the mechanical behavior of extruded ceramic Raschig rings. It is impossible to simultaneously improve the compressive strength and Weibull modulus of rings with just one of the abovementioned binders. The combination of binders roughly doubles the strength and reliability of rings compared to those of rings prepared with clay only. The mixture design method was successfully applied to determine the optimum combination of binders. It enables a mathematical description of the compressive strength as well as the Weibull modulus as a function of the binder fractions. Synergic interaction between dry strength, characteristic strength and Weibull modulus highlighted the suitable area for mixing of the binders in which the optimum mechanical properties were achieved for manufacturing reliable ceramic Raschig rings.

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