Effect of nepheline syenite particle size on diametrical compression strength and reliability of extruded ceramic Raschig rings used in packed towers

AMIN SALEM^{1,2*}, NAZILA ROSTAMI¹

¹Mineral Processing Research Center, Department of Chemical Engineering, Sahand University of Technology, Tabriz, Iran

²Center of Excellence for Color Science and Technology, Tehran, Iran

*Corresponding author: Tel: +984123459159, Fax: +984123443355, E-mail: salem@sut.ac.ir

In order to understand the effect of nepheline syenite particle size on physico-chemical properties of ceramic Raschig rings, the fluxing agent was grinded at different milling times. The compositions were prepared by blending the illitic-kaolinitic clay and pre-grinded particles. The rings were shaped by a laboratory extruder and then were sintered at 1200 °C. The mechanical reliability of sintered specimens was mathematically described by Weibull theory and the effect of pre-grinding of fluxing agent on Weibull modulus was evaluated by measuring the diametrical compression strength. Weibull modulus and strength were the criteria for selecting the suitable particle size range of nepheline syenite. It was found that the pre-grinding of nepheline syenite acts as fairly strong parameter on microstructure of rings. The investigation concludes that reliable rings can be fabricated if the particle size of nepheline syenite is arranged between 53 and 75 μm . This enhancement in reliability is valuable in packed towers.

Keywords: Ceramic Raschig ring; Extrusion, Nepheline syenite, Reliability.

Efecto del tamaño de partícula de la nefelina sienita en la resistencia a la compresión diametral y la fiabilidad de los anillos Raschig cerámicos obtenidos para relleno de torres

Para conocer el efecto del tamaño de partícula de nefelina sienita sobre las propiedades fisicoquímicas de los anillos Raschig cerámicos, este fundente fue molido a diferentes tiempos. Las composiciones se prepararon mediante la mezcla de la arcilla caolínica illítica y las partículas pre-molidas. Los anillos se obtuvieron en una extrusora de laboratorio y luego fueron sinterizados a 1200 °C. La fiabilidad mecánica de las muestras sinterizadas se describe matemáticamente por la teoría de Weibull y el efecto de pre-molienda del fundente en el módulo de Weibull se evaluó midiendo la resistencia a la compresión diametral. El módulo de Weibull y la resistencia fueron los criterios para seleccionar el rango de tamaño de partícula adecuado de nefelina sienita para la fabricación de los anillos que se determinó estaba entre 53 y 75 μm comprobándose que influye considerablemente en la microestructura de los mismos. La fiabilidad alcanzada fue muy valiosa para la utilización de estos anillos como relleno en distintos tipos de torres.

Palabras clave: Anillos Raschig cerámicos, extrusión, nefelina sienita, fiabilidad, resistencia a la compresión diametral

1. INTRODUCTION

Packed towers are vertical columns in which the liquid and gas are contacted on packed beds as shown schematically in Figure 1. The liquid enters at the top and flows downward by gravity. On the opposite way, the gas passes upward through the packed beds. The overall effect is contact of gas and liquid. The vertical columns were filled with packing or materials which produce large surface. The liquid is distributed over and trickles down the beds, exposing a large surface to contact the gas. Packed bed should provide large interfacial surface between liquid and gas with desirable fluid-flow. Also, the bed should be chemically inert to fluids. Easy installation and handling should be considered in manufacture of beds. The purpose of packed towers used for the gas-liquid operations such as distillation and absorption is to provide contact of two fluids in order to permit interface diffusion of constituents.

Figure 1. Schema of packed tower.

The components of solutions are separated due to mass transfer. The rate of heat and mass transfer are directly depended on the interfacial surface exposed between the phases, the nature and degree of dispersion. The ceramic beds with different porosity have been used in the chemical and petrochemical applications. These materials are useful in contact with most liquids except alkali solutions and hydrofluoric acid (1). In order to fabricate the packed beds with the desirable properties, it is necessary to control starting composition, shaping and sintering steps (2). The ceramic Raschig ring is an especial type of packed beds with the equal dimensions in external diameter and height (3). The application of Raschig ring is a function of porosity as well as the specific surface area provided by the packed bed. Therefore, the defect morphology of ring should be controlled to achieve the reliable performance during the operating conditions.

The ceramic beds composed of quartz, illitic-kaolinitic clay and fluxing agents such as feldspars and nepheline syenite are considered to be one of the most complex ceramic materials. Recently, the requirements for reinforcing of ceramic beds have been increased especially in the form of Raschig ring. These requirements have been empirically investigated by Villora et al. that compared the reliability of rings fabricated by three methods of slip casting, pressing and extrusion (4). They found an empirical relationship between green shaping method and the reliability of final products. The microstructure analysis of the fracture surfaces indicated that the defects produced by the extrusion were typically uniform compared to those produced by other shaping methods. The results of investigation carried out by Salehi and Salem clearly indicated that the moisture of paste significantly influences both the diametrical compression strength and reliability of rings (5). The optimum moisture content to achieve maximum Weibull modulus was determined to be between 20 and 25 wt.%.

Physico-mechanical properties of dried and sintered ceramic Raschig rings were studied in the presence different type and content of binders by Beygi Khosrowshi and Salem (6). Diametrical compression strength and Weibull modulus were measured to evaluate the effect of binder on reliability of rings. They concluded that the addition of 0.5 wt.% polyvinyl alcohol improves the reliability of ceramic Raschig rings due to homogeneous distribution of defects. The increase in binder content yields the defects with elongated dimensions that decrease the Weibull modulus. Also, carboxymethyl cellulose and Arabic gum did not influence the Weibull modulus compared to polyvinyl alcohol.

According to the review study carried out by Carty et al., the clay based ceramics can be reinforced by three methods (7): the matrix reinforcement, particle dispersive reinforcement and reduce in porosity of ceramic body. The matrix reinforcement involves with the compressive stress acting on the glassy phase which is affected by different thermal expansion coefficients of the matrix and dispersed particles as well as precipitation of crystalline phase, such as mullite. Salehi and Salem demonstrated that Weibull modulus virtually decreases as a function of firing temperature and soaking time because of pore population, though the average diametrical compression strength may be increased by increment in sintering temperature (8). They reported that

a pronounced improvement in the reliability is achieved by sintering of rings at the high temperature and short soaking time.

For the production of ceramic body with low porosity, fluxing agents often are used to form melted phase. The diffusion of liquid phase into the interconnected pores is controlled by viscosity and surface tension of melted phase. It was reported that the presence of soda feldspar in the ceramic composition improves the flexural strength at 1200 °C compared to potash feldspar (9). On the other hand, the type of fluxing agent affects the firing and densification of ceramic body. Regarding the use of fluxing agents in ceramic bodies, some investigations have been published about the improvement of mechanical properties. Mukhopadhyay et al. reported that the limited use of talc in porcelain stoneware composition promotes the mechanical properties due to reducing total porosity (10). Rostami et al. showed that the use of nepheline syenite in appreciable amount improves the diametrical compression strength and reliability of ceramic Raschig rings (11).

The results of the previously studies on porcelain stoneware body composition indicated a limitation for using nepheline syenite in the ceramic compositions. However, the aim of the present study is to investigate the role of particle size of nepheline syenite on the diametrical compression strength of extruded ceramic Raschig ring and clarifying of the reinforcement mechanism to achieve a more effective reliability.

2. EXPERIMENTAL PROCEDURES

In the present study the effect of pre-grinding of nepheline syenite on physical - mechanical properties of ceramic Raschig rings was investigated. For this purpose the processed illitic-kaolinitic clay and nepheline syenite powders, supplied by Iranian industries, were used as raw materials. The chemical compositions of clay and nepheline syenite determined by XRF technique (Model S4 Explorer 7KP103, Bruker, Karlsruhe, Germany) are reported in Table I. The mineralogical analyses of the raw materials were determined by X-Ray diffraction (Model D8-Advance, Bruker, Germany) as shown in Figure 2. According to the mineralogical analyses, the used clay consists of kaolinite, pyrophyllite, illite and quartz. The other minerals such as calcite are also found in the small amounts. Iranian nepheline syenite consists of mainly albite, orthoclase and oligoclase. Nepheline syenite was milled by a dry jar mill and passed through the American standard sieves (Cooper Technology, UK) to prepare the following particle size ranges of fluxing agent: 75-106 μm (-140 to +200 mesh), 53-75 μm (-200 to +270 mesh), 38-53 μm (-270 to +400 mesh) and less than 38 μm (-400 mesh). The clay was chosen as a base material and 5.0 and 10.0 wt.% nepheline syenite were added to prepare the new compositions. Different particle size ranges of nepheline syenite were used in these compositions to understand the role of particle size on physical - mechanical characteristics. After the mixing of various ring compositions, 2.5 kg of each powders were wetted with 25 and 30 wt.% deionized water in order to prepare the pastes for shaping process. The pastes were left for 48 hours to obtain the materials with the homogenous humidity.

TABLE I: CHEMICAL ANALYSIS OF RAW MATERIALS (WT.%)

Oxides	Kaolin	Nepheline syenite
SiO ₂	58.00	57.91
Al ₂ O ₃	28.00	22.80
Fe ₂ O ₃	0.35	0.35
TiO ₂	<0.25	0.02
CaO	<0.50	0.82
MgO	<0.15	0.00
K ₂ O	4.50	7.51
Na ₂ O	<0.20	10.00
SO ₃	trace	0.10
Rb ₂ O	0.00	0.04
MnO	0.00	0.04
L.O.I ^a	6.00	0.00

^aLoss on ignition.

Figure 2. The XRD patterns of raw materials, A: albite, I: illite, K: kaolinite, P: pyrophyllite, O: orthoclase, Ol: oligoclase, Q: quartz

TABLE II: GEOMETRICAL AND PHYSICAL PROPERTIES OF DRY RINGS

Particle size distribution (μm)	Internal diameter (cm)	External diameter (cm)	Height (cm)	Dried density (g/cm ³)	Total porosity (%)
Reference composition, STD					
	1.48±0.01	2.46±0.01	2.54±0.03	1.61±0.01	33.2±0.4
5.0% nepheline syenite					
75-106	1.48±0.01	2.48±0.01	2.48±0.02	1.68±0.01	32.0±0.4
53-75	1.48±0.01	2.45±0.01	2.54±0.02	1.64±0.01	33.6±0.4
38-53	1.48±0.01	2.48±0.01	2.50±0.02	1.64±0.01	33.6±0.4
< 38	1.49±0.01	2.44±0.01	2.47±0.02	1.64±0.01	33.6±0.4
10.0% nepheline syenite					
75-106	1.48±0.01	2.48±0.01	2.48±0.01	1.66±0.01	34.9±0.4
53-75	1.48±0.01	2.48±0.01	2.54±0.02	1.63±0.01	36.1±0.4
38-53	1.48±0.01	2.43±0.01	2.47±0.02	1.64±0.01	35.7±0.4
< 38	1.48±0.01	2.44±0.01	2.51±0.01	1.63±0.01	36.1±0.4

Figure 3. Dry ceramic Raschig rings.

The de-airing of the pastes was carried out by using a laboratory pug mill. The rings were formed by the extrusion of body mixes through a single-screw extrusion machine, prototype, at pressure of 20 MPa and then cut them to the proper length. The shaped specimens were dried in a laboratory dryer in 110 °C, Figure 3, and the geometrical characteristics of rings are reported in Table II. The bulk density of the dry specimen was determined by the weight and geometrical dimensions. The true density also was measured by the helium pycnometer (Model Ultrapycnometer 1000, Quantachrome Ins, USA) and the total porosity was calculated for each run as a follows:

$$\text{total porosity} = 1 - \frac{\text{bulk density}}{\text{true density}} \quad [1]$$

The test specimens were heated in a laboratory electrical furnace (Model EX.1500-6L, Exciton, Iran) to 573 °C at heating rate of 5 °C/min and held 1 hour in this temperature for $\alpha \rightarrow \beta$ quartz inversion. Finally, the temperature of the furnace was increased at a rate of 10 °C/min to reach 1200 °C and held at this peak temperature for 2 hours in the air atmosphere, Figure 4. The linear shrinkage, water absorption, open and total porosity were determined by standard procedure for the fired rings (12, 13).

Figure 4. Sintered ceramic Raschig rings.

The diametrical compression strength was measured by the universal test machine (Model Zwick/Roell Z010Z, Germany). The Raschig rings were loaded using the steel compression plates at a head speed of 1mm/min. At least 20 samples were tested to measure the diametrical compression strength of Raschig rings. Weibull distribution for brittle materials such as ceramics was developed as follows (14):

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

where P_i is the probability of failure at a stress of σ_i , σ_0 is Weibull characteristic strength corresponded to the stress at which the probability of failure is 63.2%. Weibull modulus, m , controls the shape of curve, being larger as scattering degree of diametrical compression strength decreases. Therefore, the high value of Weibull modulus describes the reliable material. This parameter was determined by the least squares method, using a probability estimator of failure as reported by Salehi and Salem (15):

$$P_i = \frac{\sigma_i}{N+1} \quad [3]$$

where N is the number of measurements and i is the ranking number of diametrical compression strength, with $n=1$ for the weakest samples and $n=N$ for the strongest specimen. This statistical analysis was used to determine Weibull modulus and the characteristic strength for each set of data.

The mineralogical phases of sintered samples were identified using the X-ray diffractometer (D8-Advance, Bruker, Germany). The microstructure of the sintered specimens was observed by scanning electron microscope (SEM, Model 440I EOL, England) to better understand the effect of pore size on the diametrical compression strength. The chemical resistance of fired ceramic bodies was measured according to standard ASTM-C515 (16).

3. RESULTS AND DISCUSSION

The effect of pre-grinding of nepheline syenite on the water absorption of the rings sintered at 1200 °C is reported

in Table III for modified compositions containing 5.0 and 10.0 wt.% of the fluxing agent. In all of modified compositions, the water absorption is less than 0.50 % compared to STD composition. From industrial point of view, the suitable value was obtained, less than 0.20 %, when the particle size of nepheline syenite was reduced less than 75 μm . It can be observed that STD sample prepared without nepheline syenite shows the highest water absorption after firing in 1200 °C. The use of nepheline syenite in the composition considerably reduces the water absorption of ring even, the addition of coarse particles showed a more pronounced effect on water absorption respect to STD composition. The change in particle size of the fluxing agent, less than 75 μm , did not considerably affect the water absorption.

TABLE III: WATER ABSORPTION OF CERAMIC RASCHIG RINGS PREPARED WITH DIFFERENT PARTICLE SIZE OF NEPHELINE SYENITE

Particle size distribution (μm)	Nepheline syenite (wt.%)		
	0.0	5.0	10.0
75-106	2.30 $\pm$ 0.20	0.34 $\pm$ 0.10	0.50 $\pm$ 0.20
53-75		0.20 $\pm$ 0.10	0.17 $\pm$ 0.15
38-53		0.19 $\pm$ 0.14	0.15 $\pm$ 0.10
< 38		0.19 $\pm$ 0.10	0.17 $\pm$ 0.10

The effect of pre-grinding of nepheline syenite on the linear shrinkage is reported in Table IV. In the compositions prepared with coarse-sized particles, larger than 53 μm , a decrease in shrinkage is observable respect to STD composition. In the modified compositions prepared with fine particles, less than 53 μm , the addition of 5.0 wt.% nepheline syenite causes an increment in the shrinkage compared to the other modified compositions with the same content of fluxing agent. The shrinkage of body containing 10.0 wt.% nepheline syenite was found to increase with reduce in the particle size and it reached a maximum value in the body prepared with the particle size of 38-53 μm . When the fine particles of fluxing agent, less than 38 μm , were used in the body composition, the dimension stability reduced considerably and an expansion is observed in the rings.

TABLE IV: SHRINKAGE OF CERAMIC RASCHIG RINGS PREPARED WITH DIFFERENT PARTICLE SIZE OF NEPHELINE SYENITE

Particle size distribution (μm)	Nepheline syenite (wt.%)		
	0.0	5.0	10.0
75-106	15.2 $\pm$ 0.4	13.2 $\pm$ 0.3	10.1 $\pm$ 0.7
53-75		13.8 $\pm$ 0.4	12.9 $\pm$ 0.7
38-53		15.6 $\pm$ 0.2	14.7 $\pm$ 0.4
< 38		15.8 $\pm$ 0.2	13.7 $\pm$ 0.5

A comparison between the total and closed porosity of the specimens is performed in Table V in presence different amounts of nepheline syenite. It is interesting to note that the addition of coarse-sized nepheline syenite, larger than 53 μm , increases both of total and closed porosity compared to those for STD specimens. In both modified compositions, the total and closed porosity indicate the similar trends with particle size. The reduction in particle size of nepheline syenite causes a decrease in total porosity till reaching a minimum

TABLE V: TOTAL AND CLOSED POROSITY OF CERAMIC RASCHIG RINGS WITH DIFFERENT PARTICLE SIZE OF NEPHELINE SYENITE

Particle size distribution (μm)	Nepheline syenite (wt.%)					
	0.0		5.0		10.0	
	TP ^a (%)	CP ^b (%)	TP (%)	CP (%)	TP (%)	CP (%)
75-106	8.4±0.4	6.1±0.4	10.2±0.3	9.5±0.3	17.7±0.2	16.6±0.2
53-75			8.1±0.2	7.6±0.2	11.7±0.2	11.3±0.2
38-53			3.7±0.4	3.2±0.4	7.3±0.3	6.9±0.3
< 38			4.9±0.3	4.4±0.3	8.5±0.4	8.1±0.4

^aTP: total porosity; ^bCP: closed porosity.

valve and then it grows due to over firing of specimens. The replacement 5.0 wt.% of clay by the fine particles of nepheline syenite, less than 53 μm , produced a marked decrease in the total porosity. Similar trend is also observed in closed porosity for this composition. The relatively fine particles of nepheline syenite, 38-53 μm , deeply affected the closed porosity and produced a decrease in total porosity respect to the reference body. The longer pre-grinding of the fluxing agent, less than 38 μm , showed quite a marked increase in the total porosity of the body prepared with 10.0 wt.% nepheline syenite but, the limited addition of nepheline syenite, 5.0 wt.%, did not influence both of total and closed porosity considerably. It seems from the Table V data that the use of 5.0 wt.% nepheline syenite, with controlled particle size, in ceramic Raschig composition strongly favors the densification process, allowing to obtain sintered materials with minimum total and closed porosity but it is necessary to control the particle size of fluxing agent for firing of rings at 1200 °C compared to STD composition.

In order to evaluate the effect of pre-grinding of nepheline syenite on mechanical characteristics of rings, the diametrical compression strength was measured. The strength data were analyzed using the statistical Weibull theory that describes the probability of failure as a function of stress. It can be used for understanding the role of particle size of fluxing agent on the reliability of rings. 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 (17):

$$\frac{\sum_{i=1}^N (\sigma_i)^m \ln(\sigma_i)}{\sum_{i=1}^N (\sigma_i)^m} - \frac{1}{N} \sum_{i=1}^N \ln(\sigma_i) - \frac{1}{m} = 0 \quad [4]$$

and

$$\sigma_0 = \left[\frac{\sum_{i=1}^N (\sigma_i)^m}{N} \right]^{\frac{1}{m}} \quad [5]$$

According to ASTM C-1239 standard method the confidence bounds can be constructed for estimated Weibull modulus and characteristic strength (17). The 90% confidence bound on characteristic strength is obtained from the 5 and 95 percentile distributions. In Table VI, the lower and upper bounds of Weibull modulus and the characteristic strength are reported in the presence and absence of nepheline syenite. The confidence bounds of the characteristic strength were influenced by the amount and particle size of nepheline syenite. For all of the modified compositions the high value of strength is observed compared to that for STD composition even, if coarse particles, 75-106 μm , are added to the composition. The composition prepared using the coarse particles causes a meaningful improvement of the strength. The diametrical compression strength of composition containing 10.0 wt% nepheline syenite, is always less than that for the bodies prepared with 5.0 wt% of fluxing agent at the same condition.

TABLE VI: WEIBULL MODULUS AND CHARACTERISTIC STRENGTH OF CERAMIC RASCHIG RINGS PREPARED WITH DIFFERENT PARTICLE SIZE OF NEPHELINE SYENITE

Particle size distribution (μm)	Weibull modulus		Characteristic strength (MPa)		R ^a
	Lower	Upper	Lower	Upper	
Reference composition, STD					
	3.9	6.6	17.7	20.4	0.97
5.0 % nepheline syenite					
75-106	8.0	13.7	38.3	41.1	0.96
53-75	7.3	12.0	37.5	40.2	0.98
38-53	4.3	7.3	39.3	41.8	0.97
< 38	6.3	10.9	39.6	43.2	0.98
10.0 % nepheline syenite					
75-106	6.3	10.2	26.9	29.1	0.97
53-75	5.5	9.0	34.0	37.3	0.99
38-53	4.4	7.3	28.8	32.5	0.95
< 38	4.0	6.6	35.0	39.8	0.94

^aR: linear regression coefficient.

Figures 5 and 6 show Weibull plots for ceramic Raschig rings containing 5.0 and 10.0 wt.% of nepheline syenite prepared with different particle size ranges of fluxing agent according to Equation 2, respectively. The upper and lower values of Weibull modulus for the reference and modified compositions prepared with different particle size of nepheline syenite are summarized in Table VI. The proposed probability function indicates satisfactory adjustment between the experimental data and the calculated values. Weibull modulus was significantly affected by the pre-grinding of fluxing agent. A pronounced increase in Weibull modulus was resulted from the short pre-grinding of nepheline syenite, 75-106 μm , but in general the diametrical compression strength showed that the coarse particles of nepheline syenite is not favorable for the fabricating of ceramic Raschig rings. The body containing 10.0 wt.% nepheline syenite indicated that the fine grinding, less than 53 μm , of fluxing agent did not improve Weibull modulus as well as the reliability of rings even, this trend

Figure 5. Weibull plots for ceramic Raschig rings containing 5.0 wt.% of nepheline syenite and prepared with different particle size ranges.

Figure 6. Weibull plots for ceramic Raschig rings containing 10.0 wt.% of nepheline syenite and prepared with different particle size ranges.

did not necessarily accompany with the strength variation. Indeed, the data for compositions containing 10.0 wt.% nepheline syenite and prepared with different particle size of fluxing agent almost distributed in the wide range with an exception in the presence coarse particles, 75-106 μm . In fact, when the particle size of nepheline syenite was reduced less than 75 μm , the reliability of rings is not significantly affected by the pre-grinding of nepheline syenite. On the other hand, the rings prepared with 5.0 wt.% nepheline syenite show a minimum difference in mechanical strength in the studied range of particle size. These specimens are also characterized by rather lower scattering data compared to those prepared with 10.0 wt.% nepheline syenite at the same condition. The rings prepared by the coarse particles, 75-106 μm , indicated a maximum reliability after firing at 1200 $^{\circ}\text{C}$. For explanation of these differences in reliability, the microstructure and crystal phases should be considered that will be presented in next part of investigation.

Figure 7 shows the morphology of the defect obtained by SEM technique for STD and the ring prepared by 10.0 wt.% of coarse particles. The fracture surface of the specimen introduced the defect with small dimension compared to that for STD body which leads to decrease in the scattering strength data, as a result Weibull modulus increases significantly. Also, a considerable increase in the diametrical compression strength was found in this case due to significantly decrease in the defect dimension. The fracture surface of the ring prepared with coarse particles of nepheline syenite, Figure 8, indicates the presence of many agglomerated pores that were homogenously distributed on the fracture surface compared to those for STD body. It is responsible for consistent increase in Weibull modulus.

Figure 7. The SEM micrographs of (a) STD, (b) body containing 10.0 wt.% nepheline syenite (75-106 μm).

Figure 8. Microstructure of (a) STD, (b) body containing 10.0 wt.% nepheline syenite (75-106 μm).

The morphology of defect and pores in body containing 10.0 wt.% nepheline syenite prepared with fine particles, 38-53 μm , are indicated in Figure 9. The low value of Weibull modulus for specimens prepared with the fine particles of nepheline syenite (10 wt.%, less than 53 μm) is evident. Among all the tested conditions, the compositions containing

the fine particles, less than $53\ \mu\text{m}$, showed the lowest Weibull modulus in the presence 5.0 and 10.0 wt.% nepheline syenite. In these cases, the strength data were distributed at the wide range due to increasing the defect and pore dimensions as shown in Figure 9.

Figure 9. Morphology of (a) defect and (b) pores in body containing 10.0 wt.% nepheline syenite ($38\text{--}53\ \mu\text{m}$).

The high value of Weibull modulus in the body containing 5.0 wt.% nepheline syenite and prepared with the coarse particles is essentially due to microstructural homogeneity. The defect induced by the extrusion, Figure 10, influences the mechanical strength of the both samples prepared with the coarse, $75\text{--}106\ \mu\text{m}$, and fine particles, less than $38\ \mu\text{m}$. For these bodies, the influence of defect dimensions is prevalent. The rings prepared with fine particles of nepheline syenite are characterized by the high strength and low value of Weibull modulus. Although Weibull modulus is less than that for the rings prepared with the coarse particles of nepheline syenite but, a high strength is observed in this case. For the specimens containing the fine particles, Figure 11, the sintering temperature of $1200\ ^\circ\text{C}$ is detrimental where the expanded pores are visible, causing a decrease in the compressive strength. The expansion of isolated gas into the closed pores increases the pores dimensions when the fine particles were used in preparation of composition. The presence of fine particles in composition can not decrease closed porosity and produces the pores with the large diameters due to pressure of gas isolated in closed pore that contributes to

Figure 10. The SEM micrographs of bodies prepared with 5.0 wt.% nepheline syenite and different particle size ranges (a) $75\text{--}106\ \mu\text{m}$ and (b) less than $38\ \mu\text{m}$.

Figure 11. Morphology of pores for bodies prepared with 5.0 wt.% of nepheline syenite and different particle size ranges (a) $75\text{--}106\ \mu\text{m}$ and (b) less than $38\ \mu\text{m}$.

negatively influence Weibull modulus. Therefore, this result can be attributed to i) reduce in the defect dimensions of ring prepared with the coarse particles of nepheline syenite and ii) the microstructural homogeneity with decrease in pore size of body. From this point of view, the coarse particles of nepheline syenite, $75\text{--}106\ \mu\text{m}$, can be considered as a suitable range to achieve the reliable ceramic Raschig rings.

Figures 12 and 13 show the XRD patterns of ceramic Raschig rings prepared with different particles of nepheline

Figure 12. The XRD patterns of sintered ceramic Raschig rings containing 5.0 wt.% nepheline syenite and prepared with different particle size ranges, M: mullite and Q: quartz.

Figure 13. The XRD patterns of sintered ceramic Raschig rings containing 10.0 wt.% of nepheline syenite and prepared with different particle size ranges. M: mullite and Q: quartz.

syenite in the presence 5.0 and 10.0 wt.% of fluxing agent. The phase transformation from kaolinite to mullite is observed in the XRD patterns. The glass phase was also found in all of the bodies that simultaneously formed with mullite crystals. Other research groups have also reported this finding and observed in clay based ceramics (8, 11). Chemical reactions that occur during the firing process of clay based ceramics depend on the type of raw materials in the ceramic body, but the basic reaction step can be outlined as follows: Kaolinite crystals contain hydroxyl groups, and the dehydroxylation of these groups to form metakaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) occurs at 400-650 °C. Metakaolin transforms to spinel type structure and amorphous free silica at 950 to 1000 °C. The spinel phase is a non-equilibrium unstable phase that certainly transforms to mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) above 1075-1200 °C. The content of mullite crystals grows and influences the mechanical strength of the ceramic body. Since the melted phase dissolves quartz, the peak intensity significantly decreases after sintering in 1200 °C. The intensity of mullite and quartz peaks appear to be high as the particle size of nepheline syenite is shifted to less than 75 μm . It should be note that these changes in the crystalline phases influence the mechanical strength of rings.

The variation in the XRD patterns can be attributed to dissolving of mullite and quartz in melted phase in other cases. According to the results reported by Esposito et al. even, 5.0 wt.% of nepheline syenite produces a more amount of glassy phase than reference composition fired at the same conditions (11). This result shows that the crystalline phases such as mullite and quartz which are unstable in alkali oversaturated glassy matrix decompose more easily. By comparing the XRD patterns, it is clearly observed that the coarse particles of nepheline syenite, 53-75 μm , yields a much higher content of crystalline phases while the intensity of mullite and quartz are not very different in other detected cases. The increase in nepheline syenite content promotes the glass phase formation. This phenomenon is obvious in specimens prepared with fine particles.

In the fact for this class of ceramics, the sintering step proceeds through development of a viscous phase that gradually diffuses into the voids among the particles, leading to the densification of body. The viscous flow is driven by capillary forces generated by the fine open pores. During cooling, the liquid phase forms the glassy phase which surrounds the minerals, giving a final product in which the residual and new crystalline phases are embedded in a rigid glassy matrix. Because of the high viscosity of silica rich liquid, bubbles of gas developed during the firing can be trapped in the bulk of materials.

TABEL VII: WEIGHT LOSS OF CERAMIC RASCHIG RINGS PREPARED WITH DIFFERENT PARTICLE SIZE OF NEPHELINE SYENITE

Particle size distribution (μm)	Nepheline syenite (wt.%)		
	0.0	5.0	10.0
75-106	1.30±0.20	0.60±0.20	0.04±0.04
53-75		0.13±0.05	0.11±0.05
38-53		0.39±0.04	0.12±0.05
< 38		0.05±0.04	0.09±0.02

Behavior of the chemical resistance of rings was studied according to standard ASTM C515 (16) as reported in Table

VII. These results are point out that the value of weight loss of the rings prepared with different content of fluxing agent did not exceed than 0.6 %. It is observed that the value of weight loss decreases with addition of nepheline syenite. These variations are much more marked for ring prepared with 10.0 wt.% nepheline syenite. From industrial point of view, the weight loss of rings should be lower than 0.20 %.

By considering the suitable values of weight loss, strength and Weibull modulus, it is found that the optimum particle size range of nepheline syenite for manufacturing ceramic Raschig ring is 53-75 μm . Also, the amount of fluxing agent should not be exceeded 5.0 wt.%. The main reason for the selection of this range is due to producing minimum open porosity, high content of crystalline phases and the uniformly distribution of pores in the ceramic body.

To compare the effects of nepheline syenite and moisture content of the paste on the mechanical properties of ceramic Raschig rings, the unreliable body containing 5.0 wt.% nepheline syenite was selected and two pastes, containing 25 and 30 wt.% water were shaped by the extrusion. The results of mechanical tests are reported in Table VIII. Though, the diametrical compression strength was not considerably affected by moisture content but, Weibull modulus was significantly improved. According to the previously study reported by authors (5) the improvement in the reliability of rings can be achieved by preparing the paste with the humidity of 25 wt.%.

TABEL VIII: WEIBULL MODULUS AND CHARACTERISTIC STRENGTH OF CERAMIC RASCHIG RINGS PREPARED WITH DIFFERENT CONTENT OF MOISTURE

Moisture (%)	Weibull modulus		Characteristic strength (MPa)		R ^a
	Lower	Upper	Lower	Upper	
25	7.3	13.2	41.1	44.5	0.96
30	4.3	7.3	39.3	41.8	0.97

^aR: linear regression coefficient.

4. CONCLUSIONS

The effect of pre-grinding of nepheline syenite on the sintering, mechanical strength and chemical resistance of ceramic Raschig rings was evaluated. Furthermore, to clarify the effect of particle size of fluxing agent on the reliability of extruded rings, the diametrical compression strength data were analyzed by Weibull statistical theory and the experimental results lead to the following conclusions:

The presence coarse particles of nepheline syenite, 75-106 μm , in the composition improves the diametrical compression strength if 5.0 wt.% of fluxing agent is used. This limitation of particle size positively influences the morphology of defects and pores in which the maximum strength is obtained. The diametrical compression strength of Raschig rings are close to 40 MPa in the presence 5.0 wt.% nepheline syenite but, the reliability of rings described in term of Weibull modulus can be strongly improved by addition of coarse particles 75-106 μm of the fluxing agent. Though the increase in particle size of nepheline syenite improves the strength and reliability of rings but, the particles arranged in 53-75 μm was selected as a suitable limitation because it correlates the maximum chemical resistance.

ACKNOWLEDGMENT

The authors wish to thank Iranian National Petrochemical Company and Petrochemical Research and Technology Company for their contribution for supporting of this investigation.

REFERENCES

1. R.E. Treybal, Mass transfer operation, McGraw-Hill Publishing Co, 3rd ed., Tokyo, Japan, 1980
2. J.R. Reed, Introduction to principles of ceramic processing, 2nd ed., John Wiley & Sons, New York, USA, 1995
3. W.L. McCabe, J.C. Smith, P. Harriott, Unit operations of chemical engineering, 6th ed., McGraw-Hill, New York, USA, 2001
4. J.M. Villora, P. Callejas, M.F. Barba, C. Baudin, Statistical analysis of the fracture behavior of porous ceramic Raschig ring, *J. Eur. Ceram. Soc.*, 24, 589-94, (2004)
5. M. Salehi, A. Salem, Effect of moisture content on extrusion process of kaolinitic-illitic clay in manufacturing of ceramic Raschig ring, *J. Mater. Proc. Tech.*, 200, 232-237, (2008)
6. Y. Beygi Khosrowshi, A. Salem, A view on organic binder effects on technical properties of ceramic Raschig rings, *Bol. Soc. Esp. Ceram. V.*, 49, 5, 335-342 (2010)
7. W.M. Carty, U. Senapti, Porcelain – raw materials, processing, phase evolution, and mechanical behavior, *J. Am. Ceram. Soc.*, 81, 3-20, (1998)
8. M. Salehi, A. Salem, Statistical analysis of compressive strength data of ceramic Raschig rings fabricated by an extrusion process using a Weibull distribution, *J. Ceram. Process. Res.*, 9, 167 -171, (2008)
9. S. Kr. Das, K. Dana, Differences in densification behavior of K and Na-feldspars containing porcelain stoneware tiles, *Thermochim. Acta*, 406, 199-206, (2003)
10. T.K. Mukhopadhyay, M. Das, S. Ghosh, S. Chakrabarti, S. Ghatak, Microstructure and thermo mechanical properties of talc doped stoneware composition containing illitic clay, *Int. Ceram.*, 29, 587-597 (2003).
11. N. Rostami, A. Salem, A. Paknjhad, Influence of nepheline syenite on mechanical reliability of ceramic Raschig rings, *Int. J. Appl. Ceram. Technol.*, 8 [2], 446-454 (2011)
12. PrEN 623-2, Methods of testing advanced technical ceramics general and textural properties, part 2: determination of density and porosity, European Standard, 1991
13. ASTM C373, Standard test method for water absorption, bulk density, apparent porosity, and apparent specific gravity of fired whiteware products, *Annual Book of ASTM Standards*, 2006
14. G. Jianghong, A new probability index for estimating Weibull modulus for ceramics with the least-square method, *J. Mater. Sci. Letters*, 19, 827-29, (2000)
15. M. Salehi, A. Salem, Influence of sintering condition on strength reliability of ceramic Raschig rings shaped by extrusion process, *Material Processing for properties and performance conference MP³*, 5, 182-184, (2006)
16. ASTM C515, Standard specification for chemical-resistant ceramic tower packing, *Annual Book of ASTM Standards*, 1995.
17. ASTM C1239, Standard practice for reporting uniaxial strength data estimating Weibull distribution parameters for advance ceramics, *Annual Book of ASTM Standards*, 2001

Recibido: 24/05/2011

Aceptado: 14/01/2013