

The British University in Egypt

**BUE Scholar**

---

Chemical Engineering

Engineering

---

11-2016

## Preparation of Nano-Size Ceramic Membrane from Industrial Waste

Shereen K. Amin

*National Research Centre, Dokki, Cairo, Egypt*

Mai H. Roushdy

*The British University in Egypt, mai.hassan@bue.edu.eg*

Chakinaz Aly El-Sherbiny

*Cairo University*

Heba mohamed abdallah

*National Research Centre, Dokki, Cairo, Egypt, heba\_nasr94@yahoo.com*

Magdi F. Abadir

*Cairo University*

Follow this and additional works at: [https://buescholar.bue.edu.eg/chem\\_eng](https://buescholar.bue.edu.eg/chem_eng)

 Part of the [Membrane Science Commons](#)

---

### Recommended Citation

Amin, Sh.K. & Roushdy, Mai & El-Sherbiny, S & Abdallah, H. & Abadir, M. (2016). Preparation of Nano-Size Ceramic Membrane from Industrial Waste. 11. 7176-7181.

This Article is brought to you for free and open access by the Engineering at BUE Scholar. It has been accepted for inclusion in Chemical Engineering by an authorized administrator of BUE Scholar. For more information, please contact [bue.scholar@gmail.com](mailto:bue.scholar@gmail.com).

## Preparation of Nano-Size Ceramic Membrane from Industrial Waste

**Sh. K. Amin**

*Assistant Professor, Chemical Engineering and Pilot Plant Department,  
Engineering Research Division, National Research Centre, Dokki, Giza, Egypt.  
Corresponding Author E-mail: [dr.shereenkamel@hotmail.com](mailto:dr.shereenkamel@hotmail.com), [sheren51078@yahoo.com](mailto:sheren51078@yahoo.com)*

**M. H. Roushdy**

*Chemical Engineering Department, Faculty of Engineering, British University, Cairo, Egypt.*

**S. A. El-Sherbiny**

*Assistant Professor, Chemical Engineering Department, Faculty of Engineering, Cairo University, Giza, Egypt.*

**H. A. M. Abdallah**

*Assistant Professor, Chemical Engineering and Pilot Plant Department, Engineering Research Division,  
National Research Centre, Dokki, Giza, Egypt.*

**M. F. Abadir**

*Professor, Chemical Engineering Department, Faculty of Engineering, Cairo University, Giza, Egypt.*

### Abstract

Industrial ceramic wastes are becoming an increasing problem worldwide. Recently, this problem has attracted social concern due to the growing amounts of waste despite the measures and precautions that have been taken worldwide aiming at managing such wastes. One promising solution that has been recently researched consists incorporating such wastes in ceramic bodies which besides minimizing the waste load often improve the quality of the ceramic body.

Roller kilns used in the production of ceramic tiles are routinely ground to remove traces of contamination. The fine ground powder is usually discarded as a useless waste. In the present paper, the kiln rollers grind waste is recycled and used as raw material in the production of stable, highly active nano-size ceramic membranes for use in water desalination. The powder waste was analyzed by XRF for chemical composition, XRD for mineralogical composition, DTA and TGA for thermal analysis, TEM, and particle size distribution. The support ceramic membrane samples were formed into disks by using organic binder (PVA) with different concentrations, and pressing at 25 MPa, drying then firing at temperatures ranging from 1100 to 1300 °C for 1, 2, and 3 hours soaking time. The following properties were then investigated: Apparent and closed porosity, bulk density, water absorption. Preliminary trials for water flux and salt rejection were also performed on salty water.

**Keywords:** ceramic wastes, ceramic membranes, water desalination.

### INTRODUCTION

In the past four decades roller kilns have become the main firing device in the manufacture of ceramic tiles as well as several other products such as flat dinnerware, small insulating refractories and other ware. A roller kiln consists of a set of stationary parallel horizontal rollers spaced at a

convenient distance and situated in a row along the length of the kiln.

One of the environmental problems associated with the operation of such kilns is the periodic need to grind the kiln rollers. These are often fabricated from high alumina clays and are continuously contaminated by either flow of glaze from tile edges or depositions of alkali salts by condensation from vapor phase. Thus using this waste will help in solving an environmental problem due to increasing amount of this fine waste [Roushdy et al., 2014].

On the other hand, the application of micro-filtration and ultra-filtration for water treatment has become standard procedure during the last two decades. Actually using ceramic membrane instead of the common steps (coagulation, sedimentation and filtration) has proved to be more advantageous and effective [Gaulinger, 2007]. The use of ceramic membrane has several advantages such stability at high temperature, high pressure, chemical attack and pH resistance.

Some previous research have been made concerning the use of industrial inorganic waste in the fabrication of ceramic membranes such as the work of Jedidi et al. [2009, 2011] who prepared a membrane support using fly ash after being mixed with organic additives and water. They shaped and fired the resulting mix to 1125 °C to obtain a membrane having an average pore size of 0.25 µm with reasonable mechanical strength. Also, Fang et al. [2013] produced a low cost ceramic membrane by using coal fly ash. On the other hand saw dust was used as pore former in a ceramic type membrane devised by Bose and Das [2013, 2015]. Recently, Tolba et al. [2015] prepared an efficient adsorbant membrane based on amorphous nano-silica particles obtained from rice husk. Since water scarcity is a critical concern in many areas worldwide, there is an increasing concern about the problems that arise due to water shortage and the possible solutions available [Hanjra and Qureshi, 2010].

## RAW MATERIALS AND EXPERIMENTAL METHODS

Two raw materials were used in that work:

- First, kiln rollers hazardous fine waste, kindly supplied by Ceramica Prima Company, Sadat city.
- Second, Polyvinyl alcohol (PVA) kindly supplied by Oxford Company (India) of average molecular weight = 115000 and viscosity 25-32 cP. A typical TG analysis of PVA showed that it decomposes completely at about 500 °C [Gilman et al., 1995].

The chemical analysis of fine ceramic waste was assessed using XRF. The equipment used was AXIOS, Panalytical 2005, Wavelength Dispersive (WD-XRF) Sequential Spectrometer, installed at the National Research Center, Cairo.

The phase composition was obtained by XRD analysis using BRUKER D<sub>8</sub> advanced computerized X-Ray Diffractometer apparatus (At the Center Metallurgical Research and Development Institute, Cairo) with mono-chromatized Cu K<sub>α</sub> radiation, operated at 40 kV and 40 mA.

This was supplemented by TEM identification. The equipment used was located at the National Research Center, Cairo (JEOL, JEM-2100 Plus instrument).

On the other hand, thermal analysis was used to follow up possible thermal changes in the prepared mixtures (TGA and DTA). (NETZSCH STA 409 C/CD", installed at the Center of Metallurgical Research and Development Institute).

The particle size distribution of fine waste was obtained with a BT-2001 Laser Particle Size Analyzer (conforming to ISO 13320/2009). It is present at the Center of Metallurgical Research and Development Institute (CMRDI Helwan, Cairo). Finally, the powder density was determined using the density bottle method [ES 1859-2/2006] while the sintering parameters (bulk density, apparent porosity, water absorption) were determined according to ASTM C 373 [2014]. Each ample consisted of three specimens and the average value was taken each time.

## PREPARATION OF SUPPORT MEMBRANE SPECIMENS

The preparation of support membrane specimens was carried out as follows:

- a) A fine waste powder of 10 grams was mixed with polymer with 15 % by weight of PVA with a certain concentration.
- b) Cylindrical specimens of diameter 50 mm were formed by pressing mixtures in molds using a laboratory hydraulic press under uniaxial pressure = 25 MPa.
- c) Membrane specimens were dried on two steps using a laboratory dryer. First at 70 °C for 6 hours, then at 110 °C for another 6 hours.
- d) Membrane specimens were fired using a laboratory muffle furnace, at five different temperatures (1100, 1150, 1200, 1250, and 1300 °C), for (1, 2, and 3) hours soaking time at each temperature. These fifteen firing conditions were applied to all of the prepared membranes with different PVA concentrations varying from 2 to 8 % PVA. The firing schedule was designed to simulate roller kiln operation as follows:

- i. Fast increase of temperature from room temperature to 450 °C and maintained for 1 h at this temperature to eliminate the organic binder (PVA).
- ii. Fast increase of temperature to the required firing temperature and soaking time, then cooling down to room temperature.

The dimensions of the formed membranes were determined using a digital Vernier caliper. Also, the mass of membranes were determined using a digital balance displaying its readings up to 0.01 g accuracy.

## RESULTS AND DISCUSSION

### *Chemical composition of ceramic waste*

Table (1) shows the chemical analysis of the ceramic waste as determined by XRF.

**Table 1:** Chemical composition of ceramic waste

Constituents ( wt. % )	Waste
SiO <sub>2</sub>	23.55
Al <sub>2</sub> O <sub>3</sub>	63.86
Fe <sub>2</sub> O <sub>3</sub>	1.16
TiO <sub>2</sub>	0.33
ZrO <sub>2</sub>	3.45
CuO	0.22
ZnO	0.22
MgO	1.96
CaO	3.51
Na <sub>2</sub> O	0.8
K <sub>2</sub> O	0.48
HfO <sub>2</sub>	0.18
Co <sub>3</sub> O <sub>4</sub>	0.12
P <sub>2</sub> O <sub>5</sub>	0.17
LOI	0.002
<b>Total</b>	<b>100.012</b>

In this table, alumina is the main component rather than silica. This is due to the fact that the rollers used in the kiln are of the high alumina type. Also an almost zero loss on ignition was observed.

### *Mineralogical of ceramic waste*

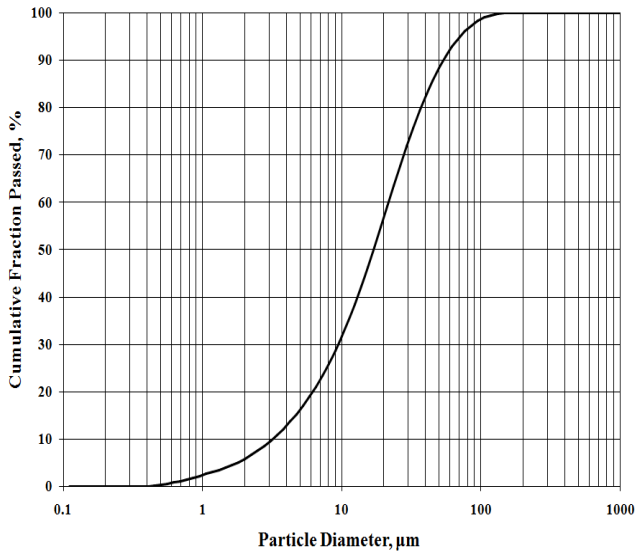
The XRD pattern of ceramic waste showed it to be constituted from the following phases: Mullite (Al<sub>2.72</sub>Si<sub>1.738</sub>O<sub>4.864</sub>), Corundum (Al<sub>2</sub>O<sub>3</sub>), Anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>), and Gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>).

### *Thermal analysis of ceramic waste*

The TG-DTA traces of the ceramic powder, upon heating in air at 10 °C/min, didn't display any peaks except a small endothermic peak coupled with about 0.8 % weight loss at 110 °C presumably associated with the loss of humidity.

**Particle size distribution of ceramic waste**

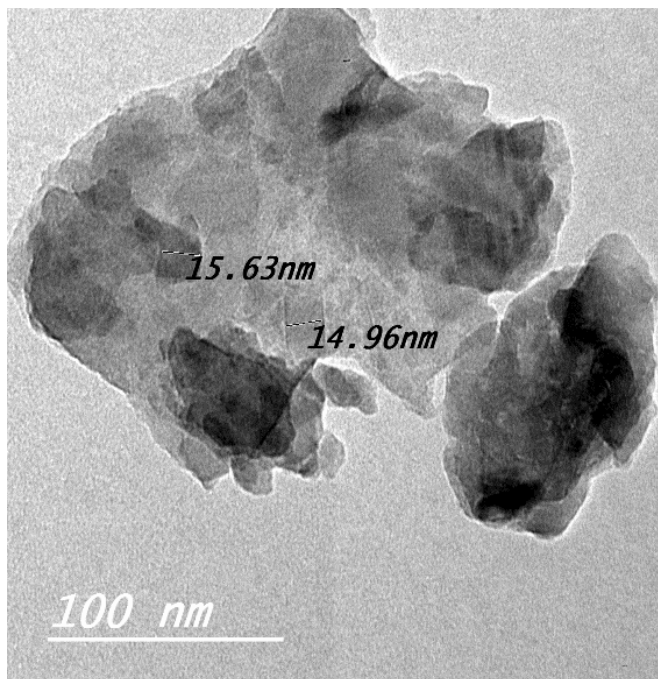
Figure (1) shows the particle size distribution of the ceramic powder waste. It reveals that the minimum particle size is about 300 nm while its maximum value is about 200 μm. The median particle size  $D_{50\%}$  was about 17 μm.



**Figure 1:** Particle size distribution of ceramic waste

**TEM investigation**

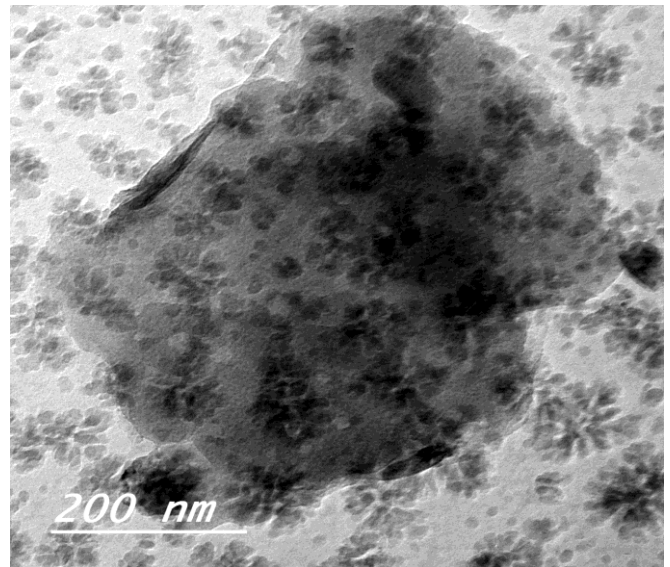
Despite the fact that particle size analysis has revealed a minimum particle size of about 300 nm it was possible to detect nano-particle size using TEM imaging. Figure (2) shows such a micrograph suggesting the presence of core-shell structure, presumably an alumina shell enclosing a mullite core.



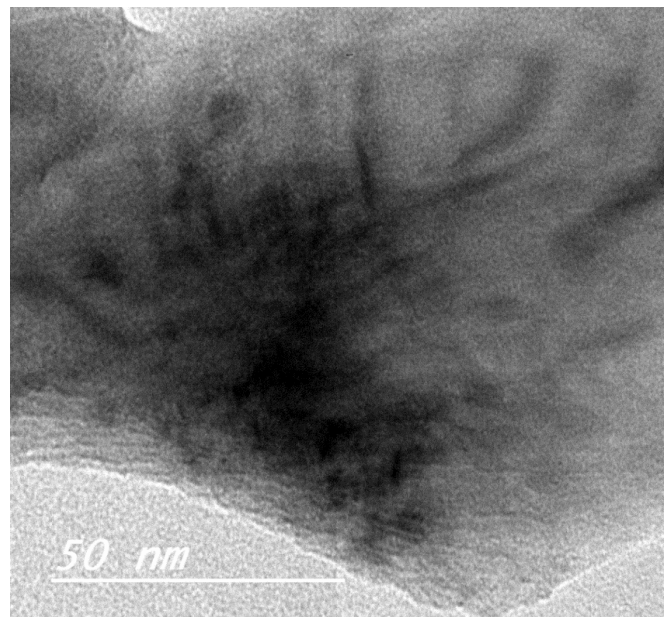
**Figure 2:** Core-shell structure

In Figure (3), Rosette-like segregations are visible when coarser particles are observed, composed of different numbers of branches. This is due to crystals having the same morphology grown from some solid inclusions randomly distributed in the interior. These inclusions are normally due to minute amounts of glaze spilling on the roller surface as tiles move through the kiln. Due to grain growth, these crystals form rosette-like, almost spherical crystals. This structure is favored by the uniform temperature at which a roller is exposed during the kiln operation [Molenaar et al., 1986; Schulze et al., 1995].

On taking a roller off the kiln to be ground to remove surface inclusions, the grain growth mechanism comes to a stop favoring the appearance of some dendritic structure that was detected in some micrographs (Figure 4).



**Figure 3:** Rosette type structure of coarse waste particles



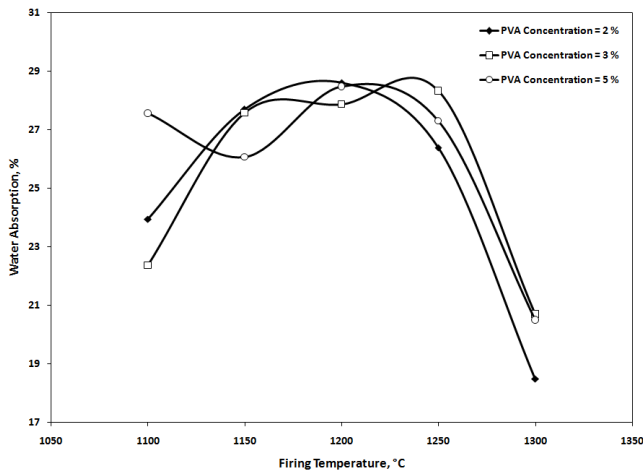
**Figure 4:** Development of dendrites within waste powder particles

**Powder density**

The density of high alumina waste has been determined using the density bottle method and repeating the procedure three times to take the mean value. This gave a powder density of: 3.14 g/cm<sup>3</sup>.

**Water absorption**

The effect of firing temperature on the percent boiling water absorption was investigated for different percentages of PVA added. Actually, the soaking time at different temperatures did not play any role in assessing that effect. This was revealed from the similar curves obtained on soaking at 1, 2 and 3 hours. Figure (5) shows the results obtained at soaking time = 1 hour.



**Figure 5:** Effect of firing temperature on percent water absorption

It can also be noted that the percent PVA did not seriously affect the shape of the curves. This is expected in view of the fact that the sintering temperatures used are much higher than that of the decomposition of the alcohol.

Water absorption initially increases in most cases up to about 1200 °C implying an increase in open pore size presumably due to dilatation of samples. After that temperature sintering sets in and a radical decrease in water absorption is observed as temperature reaches 1300 °C. The minimum value of water absorption is about 18 % in all cases irrespective of soaking time or PVA content.

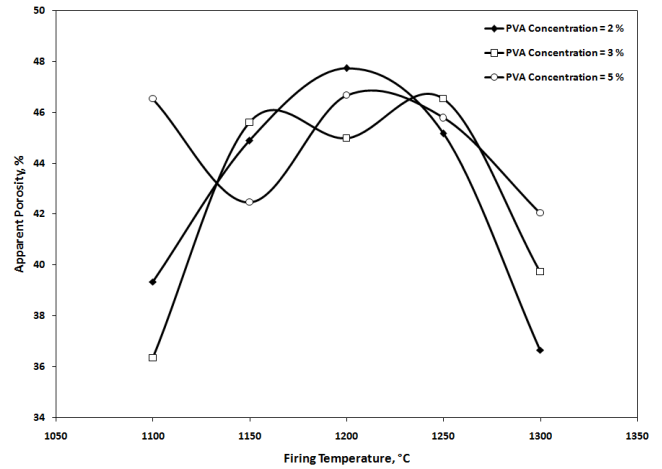
**Apparent porosity**

The behavior is very similar to that of water absorption, both being closely related. The maximum porosity was obtained on firing at 1200 °C (47-48 %) while the minimum porosity was obtained on firing at 1300 °C for three hours (33 %). Figure (6) shows the results at 1 hour soaking time.

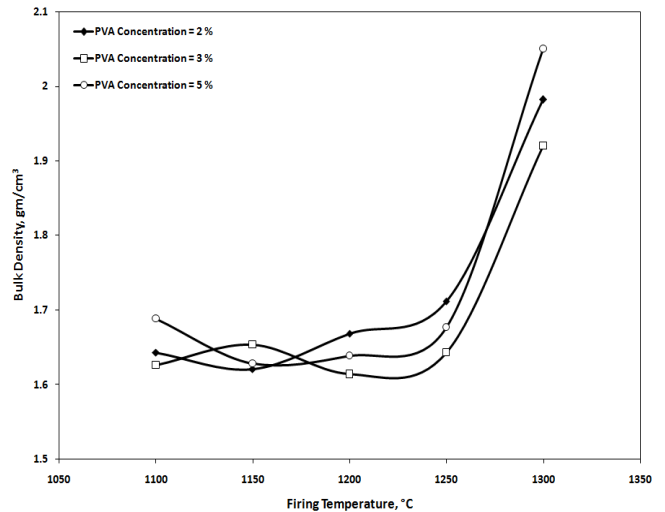
**Bulk density**

Bulk density actually depends on two factors: the total porosity of the body and its true density. The true density practically remains constant on firing as evidenced by the TGA trace. So, the total porosity of the body will influence its bulk density in an inverse way. The values of bulk density are

solely influenced by firing temperature. These simply tend to increase on raising temperature to reach a maximum value of about 2.05 g/cm<sup>3</sup> at 1300 °C. Figure (7) shows the results obtained on soaking for 1 hour.



**Figure 6:** Effect of firing temperature on percent apparent porosity



**Figure 7:** Effect of firing temperature on bulk density

**Closed porosity**

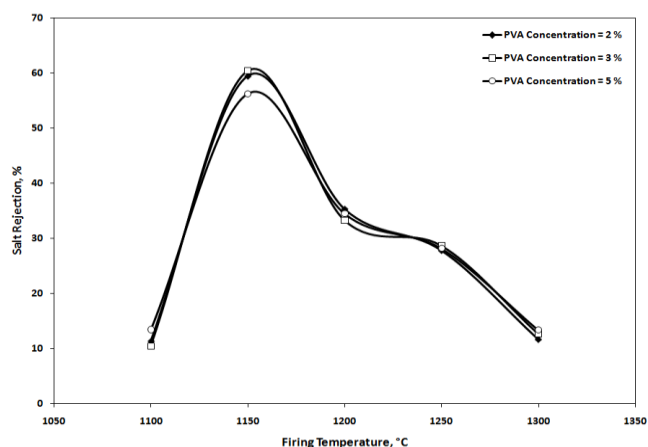
Recalling that the powder density of the waste = 3.14 g/cm<sup>3</sup>, this value corresponds to a total percent porosity of  $100 \times (1 - \frac{2.05}{3.14}) = 34.7 \%$ . The corresponding value of minimum open porosity was about 33 %, implying that there is only negligible closed porosity (1.7 %) even on firing at 1300 °C. The fact that most pores remain in their open state is essential in assessing the possibility of using this waste as micro or nano-filtration medium.

At the minimum apparent porosity of 48 %, the bulk density =  $1.6$  to  $1.65$  g/cm<sup>3</sup>, corresponding to a total porosity of  $100 \times (1 - \frac{1.6}{3.14}) = 48-49 \%$ , revealing that practically no closed pores are present on firing below 1200 °C. It was therefore decided

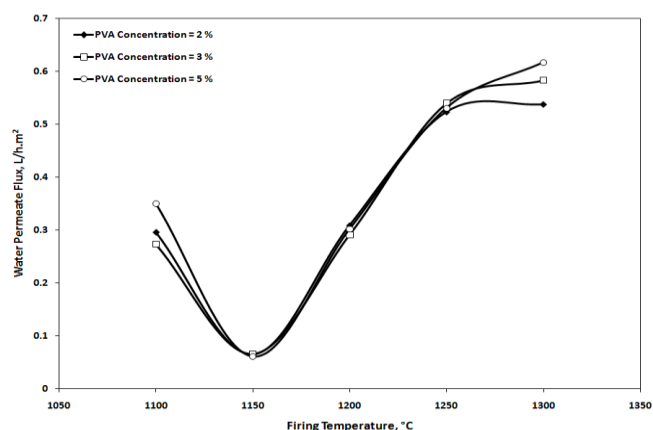
to limit the firing temperature to 1150-1200 °C to obtain the maximum amount of open pores at the same time securing a reasonable mechanical strength for the prepared bodies.

### Preliminary investigation for permeate water flux and salt rejection

Preliminary tests were undergone to investigate the viability of the prepared membranes. This effort will be concluded in a coming paper after hydrothermal treatment of raw materials. As shown in Figures (8) and (9), a preliminary experiment was done using sea water passed through the membrane. The maximum percent salt rejection was 55-60 % using for support a ceramic membrane prepared at firing temperature 1150 °C and soaking time 1 hour; the permeate flux was quite low due to the small pore size; this indicates that this ceramic membrane support can provide a promising performance after coating or after hydrothermal treatment of raw materials whereby a nano-size powder can be obtained.



**Figure 8:** Salt rejection for support ceramic membranes fired at 1150 °C



**Figure 9:** Water permeate flux for support ceramic membranes fired at 1150 °C

### CONCLUSION

The use of ceramic roller kiln waste in the preparation of ceramic membranes for water desalination was investigated.

Polyvinyl alcohol was used as binding agent. Samples were fired at temperatures ranging from 1100 to 1300 °C for soaking times up to 3 hours.

Results showed that the sintering parameters (percent water absorption, apparent porosity and bulk density) were unaffected by neither PVA level nor soaking time. The highest porosity necessary for membrane operation was obtained on soaking for one hour at 1150 °C. The percent closed porosity was negligible.

Preliminary trials undergone for water desalination suggested that the prepared membrane offered a promising cheap and effective alternative. Further trials are on their way to improve the characteristics of these membranes by hydrothermal treatment of the ceramic waste powder.

### ACKNOWLEDGMENT

This project was supported financially by the Science and Technology Development Fund (STDF), Egypt, Grant No. (10464).

### REFERENCES

- [1] ASTM C 373 [2014] "Standard test method for water absorption, bulk density, apparent porosity, and apparent specific gravity of fired white ware products, ceramic tiles, and glass tiles", Annual book of American Society for Testing of Material (ASTM), U.S.A., 15 (2), (2015).
- [2] Bose S., Das C.; "Preparation and characterization of low cost tubular ceramic support membranes using sawdust as a pore-former", Materials Letters, 110, (2013), 152-155.
- [3] Bose S., Das C.; "Sawdust: from wood waste to pore-former in the fabrication of ceramic membrane", Ceramics International, 41 (3A), (2015), 4070-4079.
- [4] ES 1859-2/2006 "Testing of physical properties for dense shaped refractory products, Part (2): determination of true density", Egyptian Organization for Standardization and Quality, Cairo, Egypt, (2006).
- [5] Fang J., Qin G., Wei W., Zhao X., Jiang L.; "Elaboration of new ceramic membrane from spherical fly ash for micro-filtration of rigid particle suspension and oil-in-water emulsion", Desalination, 311, (2013), 113-126.
- [6] Gaulinger S.; "Coagulation pre-treatment for microfiltration with ceramic membranes", TECHNEAU, (2007).
- [7] Gilman J.W., VanderHart D.L., Kashiwagi T.; "Fire and polymers II-Materials and test for hazard prevention-Chapter (11): Thermal decomposition chemistry of poly vinyl alcohol", American Chemical Society, ACS Symposium Series 599, Washington DG, (1995), 160-185.
- [8] Hanjra M., Qureshi M.; "Global water crisis and future food security in an era of climate change", Food Policy, 35, (2010), 365-377.

- [9] ISO 13320 / 2009, "Particle size analysis-Laser diffraction methods", International Organization for Standardization (ISO), Geneva, (2009).
- [10] Jedidi I., Khemakhem S., Larbot A., Amar R.; "Elaboration and characterization of fly ash based mineral supports for microfiltration and ultra-filtration membranes", *Ceramics International*, 35, (2009), 2747-2753.
- [11] Jedidi I., Khemakhem S., Saïdi S., Larbot A., Elloumi-Ammar N., Fourati A., Charfi A., Ben Salah A., Amar R.; "Preparation of a new ceramic micro-filtration membrane from mineral coal fly ash: Application to the treatment of the textile dyeing effluents", *Powder Technology*, 208, (2011), 427-432.
- [12] Molenaar J.M.M., Katgerman L., Kool W.H., Smeulders R.J.; "On the formation of the stircast structure", *Journal of Materials Science*, 21, (1986), 389-394.
- [13] Roushdy M.H., Amin Sh.K., Ahmed M.M., Abadir M.F., "Reuse of the product obtained on grinding kiln rollers in the manufacture of ceramic wall tiles", *Ceramics-Technical*, 38, (2014), 60-66.
- [14] Schulze T.P., Davis S.H.; "Shear stabilization of morphological instability during directional solidification", *Journal of Crystal Growth*, 149, (1995), 253-265.
- [15] Tolba G., Bastaweesy A., Ashour E., Abdelmoez W., Khalil K., Barakat N.; "Effective and highly recyclable ceramic membrane based on amorphous nano-silica for dye removal from the aqueous solutions", *Arabian Journal of Chemistry*, (2015), in press.