FROM ZIRCONYL CHLORIDE TO ZIRCONIA CERAMICS, A PLANT OPERATION PERSPECTIVE

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ABSTRACT

The differences between two hydrous zirconium filter cakes manufactured at pH 3 and 12 were studied and further processing consistent with industrial procedures was undertaken. The loss on drying was found to be approximately 23% for both filter cakes, however for the loss on ignition the ph 3 sample was found to have a 12% higher loss at 33%. The specific surface area (SSA) was found to be 238 m^2/g for the pH 3 sample and 312 m^2/g for pH 12. The pH 12 sample showed a linear decrease of SSA with calcination temperature and both samples achieved the same SSA after 1000 ^{o}C. The pH 3 sample took 29 hours to attrition mill to a target D90 of less than 2 μm, the pH 12 sample achieved the same target in 26 hours. X-ray diffraction revealed that both samples had crystallite sizes in the order of 30 nm and greater than 90% monoclinic phase. Both samples achieved approximately 86% theoretical density when uniaxially pressed and sintered, corresponding with 20% linear shrinkage. The pH 3 sample had greater statistical variability in most results, indicating it would be harder to control. Differences in appearance when tape cast were also noted for the two powders.

Keywords: Zirconia, Monoclinic, Industrial Processing, Tape Casting

INTRODUCTION

Stevens[1] shows that zirconia has widespread uses as an engineering ceramic, including as a dielectric in capacitors, transformation toughening agent in other ceramics such as alumina and oxygen ion sensors. Most of the literature available for zirconia focuses on the ceramic properties of the material.[2] Over recent years the Nanochemistry Research Institute (NRI) and Centre for Materials Research (CMR) at Curtin University of Technology in Western Australia have been studying the processing of zirconyl chloride to zirconia using an industrially relevant aqueous route. The route is similar to that used by a local company that is of a proprietary nature.

In previous work using Small angle X-ray Scattering, Dynamic light scattering, micro-combustion and thermogravimetric techniques the authors have found that changes in solution concentrations, added cations, agitation levels within reaction vessel and the pH of precipitation all affect the particle size of the precipitate.[3] It was shown that the pH at which the zirconium hydroxide powder precipitates influences the level of hydration of the product, as well as its behaviour in the initial stages of processing such as the filtering and drying. This has direct implications for the large scale processing of these materials. The focus of this work was to further develop the understanding of the process behaviour of zirconia powders at different pH values. The methods used have been reported previously.[4]

The calcination of hydroxides to oxides is a common industrial process, as is the use of calcination temperature to control the specific surface area (SSA) of the powder. The lower the temperature needed to obtain the required parameters the lower the cost of production.

A number of authors have noted differences in the calcination properties of zirconia dependent on its processing route each often contradicting others [5-13]. Contradictory findings are also obtained for the final phase distribution of the calcined powder. The work of Garvie [14] best demonstrates the link between crystallite size and the formation of the tetragonal or monoclinic phase of zirconia .

The particle size distribution (PSD) of the powder is extremely important and must be matched to the desired characteristics of the advanced ceramic and its processing route.[15] To achieve the required PSD size reduction processes are often used.[16] It is common to use attrition mills in the processing as they are highly efficient, thereby reducing the chances of contamination of the ceramic powder.[15]

MATERIALS AND METHODS

Powders of hydrated zirconium were precipitated from 0.81 M zirconyl chloride starting solutions at pHs of 3 and 12 as described previously.[4] Filtering and washing was carried out as previously reported[4] with the exception that all samples were left on the filter under vacuum for 2 hours.

Loss on Drying (LOD) was calculated from samples of filter cake dried in an oven at 110 °C for 24 hours (in alumina crucibles) and then cooled in a desiccator for a further 1 hour. The Loss On Ignition (LOI) was developed from the LOD samples by calcination in a muffle furnace for 2 hours at 1100 °C, after which the samples were cooled in a desiccator for 2 hours. The values reported are the mean of five samples.

Specific surface area of the powder (5 point BET) was established using a Micromeretics Gemini instrument with *Flow Prep* ©. The results are the mean of 5 determinations with the uncertainty being the standard deviation.

The samples were milled in a 01HD Union Process (Akron Ohio). Szegvari Attritor system. The attritor had a 500 ml volume with 0.8 mm diameter partially stabilised zirconia (PSZ) milling media, agitation was achieved using a PSZ attritor arm. Mill slip was made from 500 g of calcined powder obtained from 5 consecutive precipitation runs and milli-q water, the solids content was 45%. A flow through system was used with the mill slip being gravity fed to the top of the attritor from an external tank. The slip then passed through the milling chamber and a pump with an inlet at the bottom of the attritor, delivered mill slip back to the top of the external tank closing the loop. Pump speed and gravity feed rate were matched so a constant level was kept in the attritor. Sampling and testing were conducted on slip collected from the gravity feed discharge. The samples were milled until two consecutive PSD tests taken hourly returned a D90 of approximately 2μm. The use of statistical measures in particle sizing is common within the chemical powder industry the three most common measures that are used are the D90 being the 90th percentile, D50 and D10 which are both the 50th and 10th percentile respectively.

Mill slip solids content was 45% and was made from 500 g of calcined powder obtained from 5 consecutive precipitation runs and milli-q water.

Viscosity was measured using a Brookfield RV-4 viscometer at 50 RPM.

Particle sizing was obtained using a Coulter LS 320 laser particle sizing instrument.

Diffraction patterns were obtained using an in-situ powder X-Ray Diffraction (XRD) system. Oven dried samples were placed on a platinum sample well measuring 20.0 x 7.0 x 0.4 mm. The X-ray data were obtained using a X-ray diffractometer incorporating an Inel CPS-120 curved, position-sensitive detector. The angular range of the detector is 120 deg 2θ. Data were collected in the reflection mode using Cu Kα radiation operated at 35 kV and 30 mA. The XRD patterns were interpreted with the aid of Jade 6.0.3 analytical software (MDI 2003) for peak match. Phase composition and crystallite sizing was determined using Rietveld method with TOPAS Ver. 3.0 software. Crystallite size, or more correctly coherent scattering domain size, was determined from the width at half height of the [1-1-1] peaks using the Scherrer method [17]

Sample pellets for green and sintered density were formed by uniaxially pressing the powders to 200 MPa in stainless steel die using stearic acid dissolved in methanol as a die lubricant. Green and sintered densities were measured according to ASTM C20 (1992).

All samples were sintered at 1500 °C for 1 hour using a heating rate of 300 °C.hr^{-1} over the range 400-1500 °C.

The sample buttons were made using the formulation and batching procedure of Mistler and Twiname [18]. Tape was made on silicon coated Mylar film

Photographs of sample disks were taken using Pentax K10D camera with a Sigma 100 mm Macro lens. The image contrast was enhanced using Photoshop CS-Z.

RESULTS

The LOI and LOD (Table 1) show a remarkable consistency within each sample set and are consistent with values obtained by micro-combustion and DTA/TGA.[3] Previous work by the authors [3] reported that the pH 3 sample had better filtering however the ammonium chloride (NH_4Cl PDF# 07-007) was not washed out of the sample. It is evident from the present work that while it filters faster, the pH 3 sample retains more ammonium chloride and that the LOI for the pH 3 sample is higher.

SSA analysis of the dried powder prior to calcination showed clear differences; Sample pH 3 returned a SSA of 238 m^2/g and the pH 12 sample 312 m^2/g. The SSA for the two powders with increasing calcination temperature is shown in Figure 1. The pH 12 powder has a higher SSA prior to calcination and through the 600 °C to 1000 °C temperature range. At 1000 °C the SSA of the two powders converged. The pH 12 sample showed a more linear decrease in SSA with calcination temperature than the pH 3 sample. The calcined powders had different textures, the pH 3 sample was quite coarse yet friable and the pH 12 sample was mostly fine with some coarser material that broke apart in a mortar and pestle with little difficulty (Figure 2).

Table 1. LOD and LOI for pH 3 and 12 samples (all values rounded to whole numbers).

	pH 3	pH 12
LOD	56 (2)%	54 (2) %
LOI	33 (1)%	21 (1)%

Phase composition and crystallite size determination using XRD are shown in Table 2. The uncertainties developed for both the phase composition and crystallite size are estimated standard deviation (ESD) and are related to parameter fits of the model and not the variation within a given data set[19]. The uncertainties quoted in Table 2 are rounded to the nearest whole number. The two XRD data sets are shown for comparison (Figure 3) and the plot of the Rietveld refinement showing the XRD data set, refined pattern difference plot and phase identification markers

is in Figure 4. The spurious peaks evident in Figure 4 are from the platinum sample holder (PDF# 65-2868). Within the experimental limits the data sets are very similar. The crystallite sizes of the monoclinic and tetragonal forms were determined to be 36 nm and 25 nm for the pH 3 powder and 30 nm and 20 nm for the pH 12. These values are comparable with those of Garvie [14] for the occurrence of metastable tetragonal zirconia and its martensitic transformation to monoclinic above a crystallite size of 30 nm.
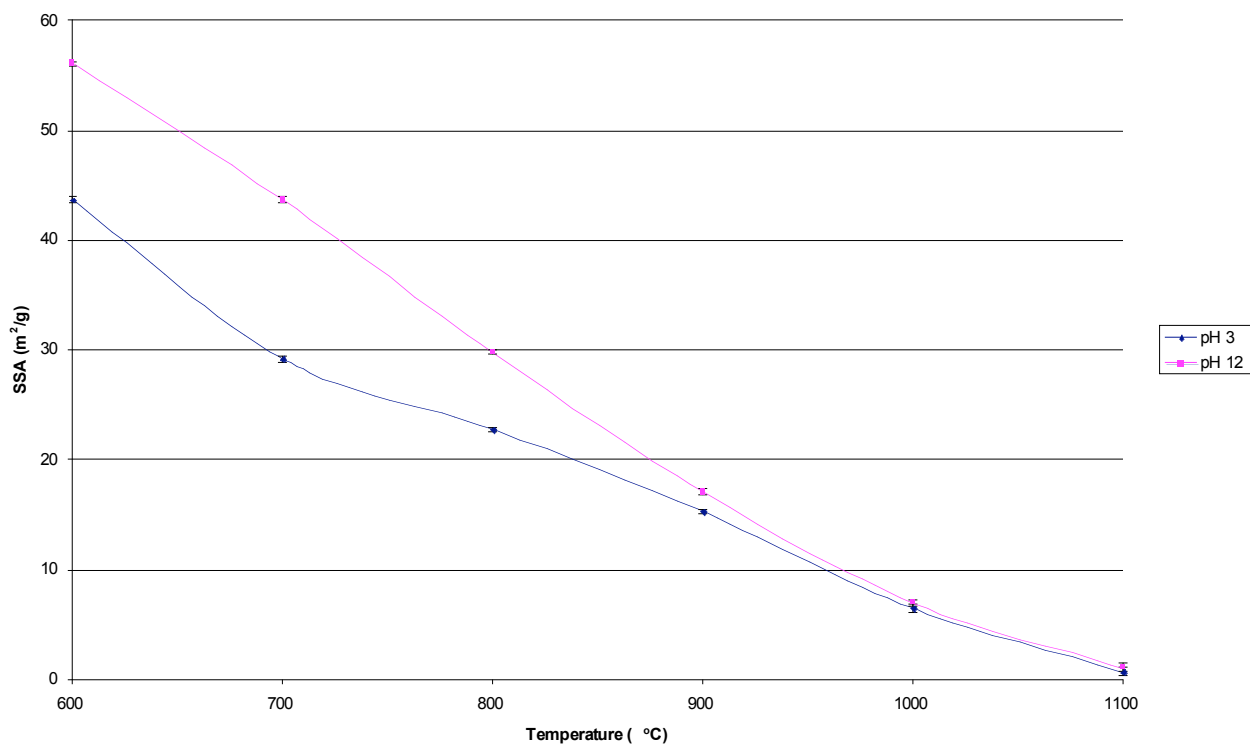

Figure 1. Specific Surface Area with calcination temperature for sample pH 3 and pH 12 (error bars are too small to be clearly seen, and indicate 1 standard deviation).
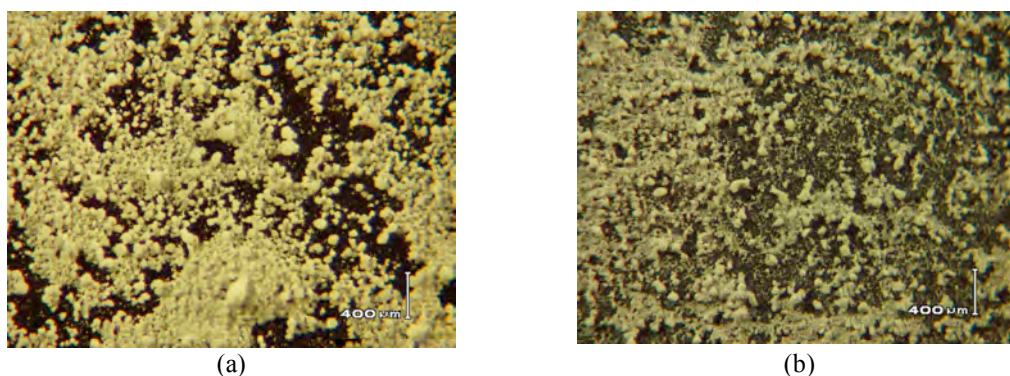

(a)   (b)

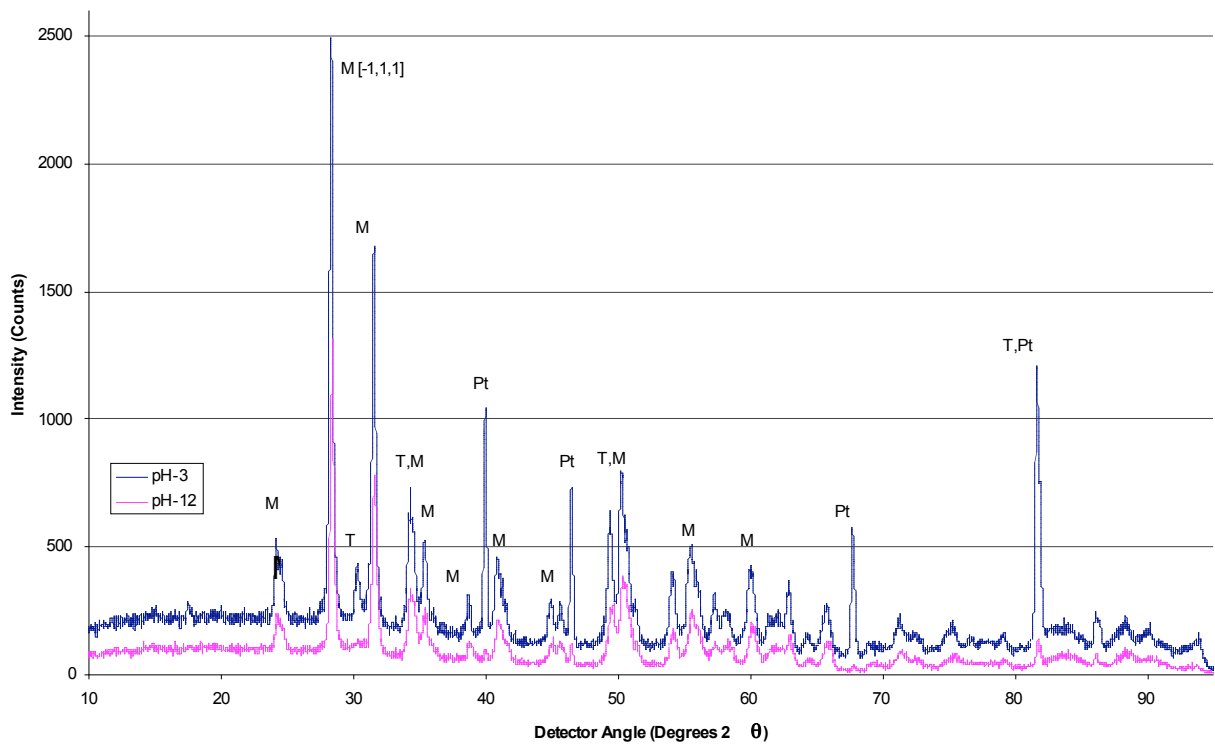**Figure 2.** Optical micrograph of powder calcined at 700 ^{o}C (a) pH 3, (b) pH 12.

Figure 3. X-ray diffraction pattern of calcined powder both pH-3 and 12 showing mostly Monoclinic Zirconia.
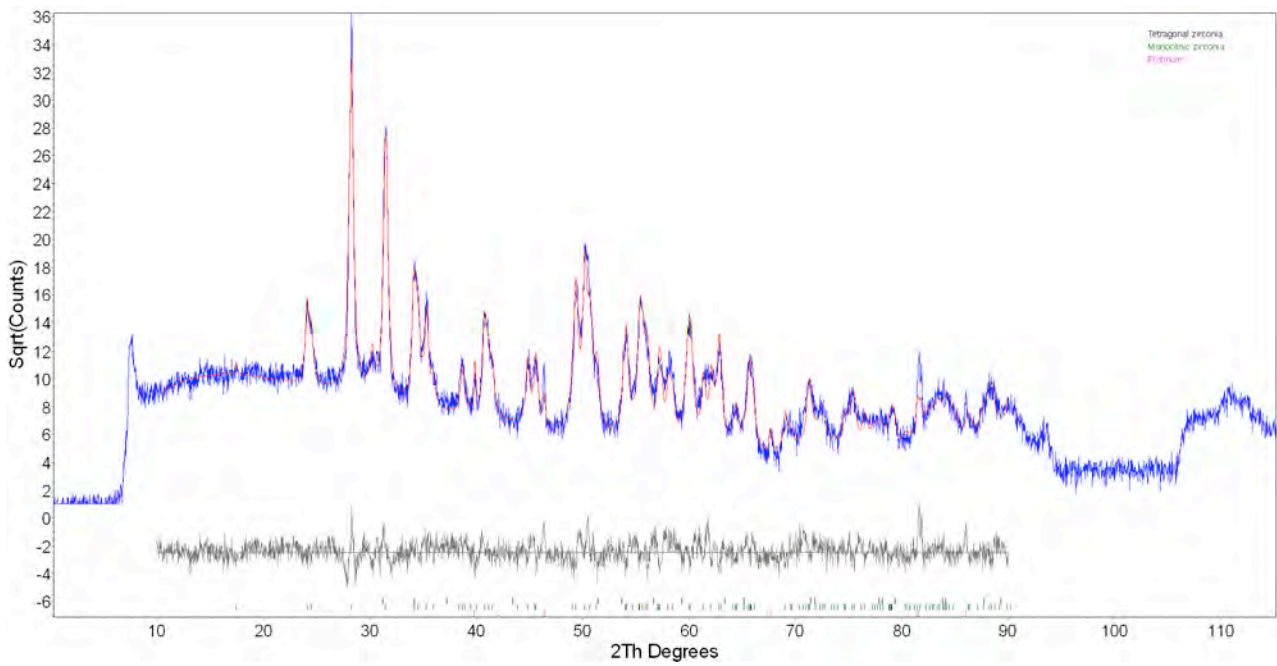

Figure 4. Topas Plot file showing refined pattern vs. data set, difference plot and phase peak markers for the Ph 12 Regions of exclusion exist above 90° 2θ and below 10.

Table 2. Phase % and Crystallite size for pH 3 and pH 12 (uncertainties are rounded to nearest whole number and are ESD)

Sample	% Phase composition		Crystallite size nm	
	Monoclinic	Tetragonal	Monoclinic	Tetragonal
pH 3	93(3)	7(4)	36(1)	25(1)
pH 12	96(5)	4(4)	30(1)	20(1)

Milling trials showed the pH 3 sample required 29 hours to reach the target D90 of 2 μm and the pH 12 sample required 26 hours (Figure 5 and Figure 6). While the difference of only three hours in the time taken to reach the target D90 appears small the overall milling responses for the two powders were significantly different. The D10 seems to plateau at 13 hours for pH 3 whilst it plateaus at 6 hours for pH 12. After 9 hours of milling the pH 12 powder has a D50 less than 5 μm with a small distribution in the particle size. This particle size is not achieved until after 16 hours for the pH 3 sample. This would suggest that the pH 12 sample would offer lower milling times for a range of target PSD in comparison too the pH 3 sample.

The viscosities of the mill slips were also measured every 4 hours (Figure 7) and are also significantly different. For the pH 12 powder the viscosity begins to increase significantly after approximately 8 hours of milling, which matches the point were the D90 drops below 5 μm. The viscosity increased until the milling was stopped. The viscosity of the pH 3 slip rises above 60 centipoises only after 24 hours of milling, even though the D90 reaches 5 μm after 16 hours. This would suggest that PSD is not the main contributing factor in the viscosity changes.
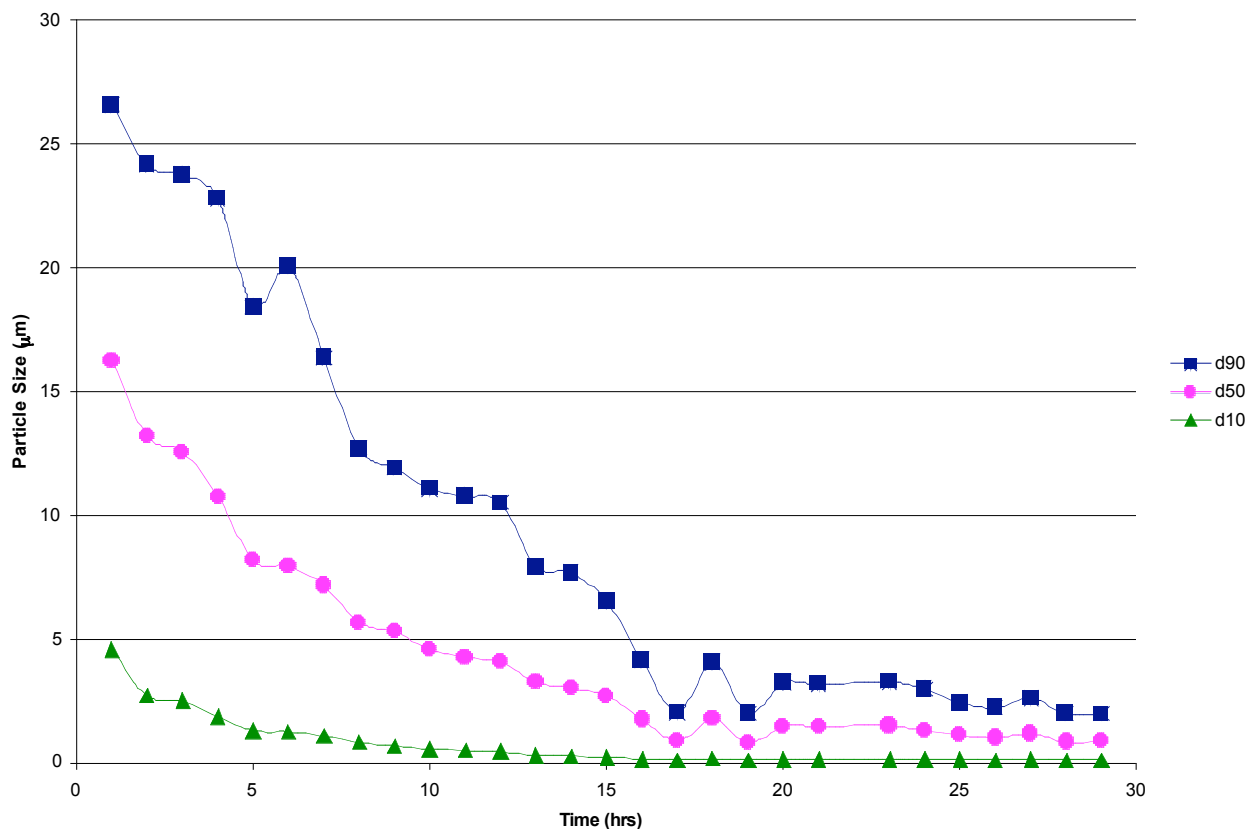

Figure 5. PSD vs Mill time for pH 3 sample.

The final sintered density and linear shrinkage of the two zirconia powders were investigated. The pH 3 sample reached 83% of its theoretical density and the pH 12 sample 88%. Theoretical density was taken to be 5560 kg.m^{-3} .[1] No distinction can be made between the two samples within the limits of the uncertainty (

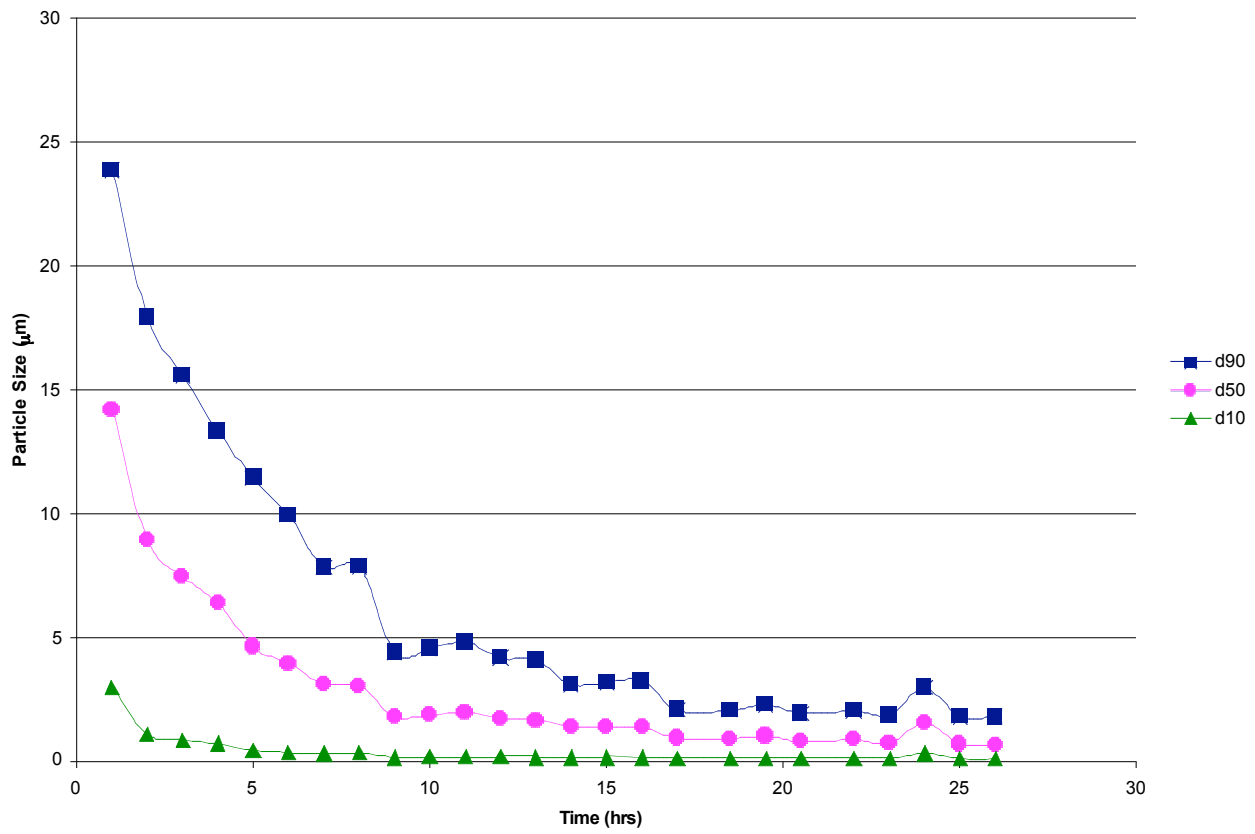Table 3). However, the pH 3 sample had a higher variability for both its density and linear shrinkage. Tape cast buttons (Figure 8) were made from each of the powders. Tape casting is common in the manufacture of electronic components that contain zirconia, such as multi-layer ceramic capacitors (MLCC) and lead zirconate titanate (PZT) piezoelectric ceramics, Although the tape casting system was kept consistent, the pH 3 sample produced opaque samples with an uneven surface flatness and striations and reduced in size less than the translucent pH 12 sample (Figure 8).

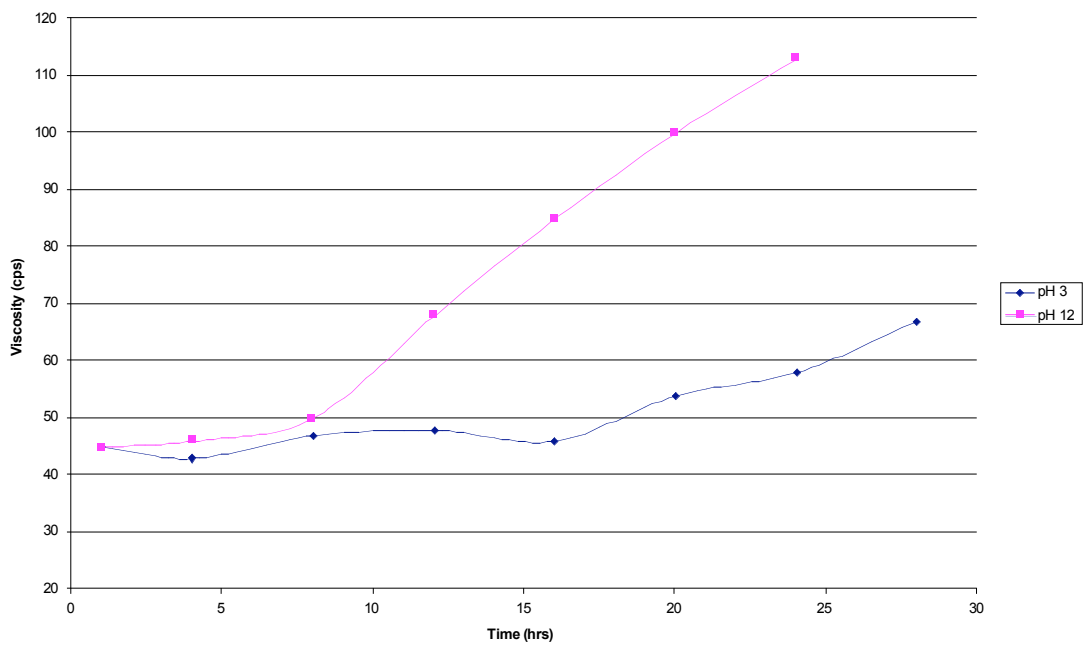**Figure 6.** PSD vs Mill time for pH 12 sample.

Figure 7. Viscosity with milling time for both pH 3 and 12 mill slip.

Table 3. % Theoretical Density and linear shrinkage for pH 3 and pH 12 sample powders.

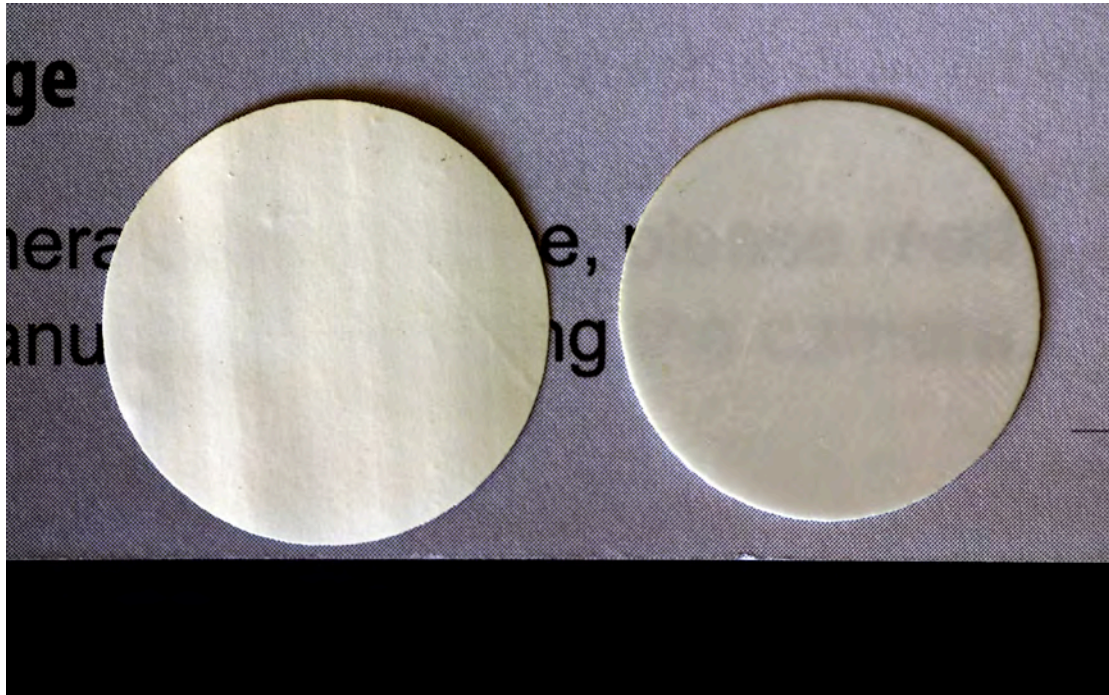|	pH 3	pH 12
% Theoretical density	83 (5)	88 (2)
% Linear shrinkage	18 (3)	21 (1)

Figure 8. Photograph of pH 3 (on the left) and pH 12 (on the right) sample disks (original lettering is 3 mm high).

CONCLUSION

The zirconia powders produced at different pH values of 3 and 12 behave differently throughout processing from hydrous zirconium precipitate to sintered ceramic. The two precipitates have almost the same LOD after filtering and vacuum drying but the pH 3 product has a higher LOI. This would have a negative effect on plant operations as the additional energy required to drive off the water increases the cost of production.

The SSA response to calcination temperature has the two powders overlapping at approximately 1000 °C. However the response by the pH 12 product is more linear and may allow for simpler fine tuning of temperature when trying to achieve a target SSA.

X-ray diffraction demonstrated that essentially the two powders were very similar once calcined, with a crystallite size in the order of 35 nm and +90% of the phase being monoclinic zirconia.

The milling curves for the pH 12 sample show a more orderly size reduction as the milling progresses that may allow target PSD to be reached in a more uniform and predictable fashion with reduced time, offering cost reduction and reduced complexity in large scale processing.

Whilst both powders produced ceramics with similar average values for theoretical density and linear shrinkage, the variability of the pH 3 samples was greater than for the pH 12 samples. This suggests that either the processing needs greater control or refinement for pH 3 materials or less predictable results will be obtained using this precursor powder. This trend was mirrored in the tape casting of the two powders with the pH 12 sample producing a better ceramic, while the pH 3 sample produced a ceramic with striations and different opacity despite the use of identical processing conditions.

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