

# The effect of processing parameters on particle size in ammonia-induced precipitation of zirconyl chloride under industrially relevant conditions.

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## Abstract

The effect of pH of precipitation, starting solution concentration, and agitation levels on the particle size of hydrous zirconia precipitates have been investigated. It was found that all three variables affect the particle size of the hydrous zirconia. The smallest particle size is produced by a 0.81 M starting solution, precipitated at pH 12 with a high agitation level. The pH of precipitation was also found to have a significant impact on the type of hydrous zirconia produced. TGA/DTA, micro combustion and TEM / EDS were used to investigate the difference in the powders produced at pH 3 and 12. This work suggests that powders produced at pH 3 will have a structure similar to  $Zr[OH]_4$  whilst those at pH 12 are more likely  $ZrO[OH]_2$ . XRD and micro-combustion suggest that the powders produced at pH 3 retained ammonium chloride whilst those produced at pH 12 did not. The filtration rates for the pH 3 product were significantly faster than that of the powders made at pH 12 which is significant in the industrial production of these materials.

Keywords: zirconia; precipitation; particle size; zirconyl chloride.

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# 1. Introduction

Recent studies of hydrous zirconia for the eventual preparation of yttria stabilised zirconia have investigated the formation of hard agglomerates produced during aqueous precipitation of hydrous zirconia precursor from zirconyl chloride solutions [1]. The formation of these hard agglomerates is industrially relevant as they are a significant impediment to the use of these materials in the large scale production of ceramic powders for purposes such as solid oxide fuel cells [2, 3]. While not the primary focus of the reported studies, literature suggests both zirconium species and precipitate particle size can be affected by the pH of precipitation, concentration and agitation rate [4, 5]. These properties are crucial in the industrial processing of these powders as they impact on parameters such as filtration rates and rheology. These effects eventually result in processing and performance issues in the ceramics produced [1].

Larsen and Gammill [6] conducted electrometric titration studies on zirconium and hafnium using zirconyl and hafnyl chlorides as the base solutions. They produced tables and curves showing precipitation occurs for zirconium at pH of approximately 2 and coagulation occurred pH ~6. The hafnium curve shows little difference in the precipitation points or coagulation points from the zirconyl solution.

Later extensive work by Clearfield [4] suggested the precipitation process was a hydrolytic polymerisation, and that the precipitation occurred at a low pH and was completed before the end point of neutralisation is reached. Clearfield explains that this is due to the retention of anions by the precipitate and that the amount of anion retention is dependent on pH, decreasing as the pH of precipitation increases. It was suggested that this behaviour indicates that the precipitates should be viewed as basic salts of variable composition [4]. Larsen and Gammill [6] also postulated the formation of basic salts by zirconium compounds and used this to explain differences found between the precipitation of hafnium and zirconium with respect to chloride ion content. The range of pH values for the precipitation points for differing concentrations of chloride ions was 1.88 to 2.29 [6]. These values agree with the results of Kovalenko and Bagdasaov [7] who conducted dissolution studies on what they call solid  $Zr(OH)_4$  where they found that dissolution in nitric acid occurs at a pH of 1.9 and increases up to a pH of 1.8. They suggest that the precipitation must occur at these pH values as well. The solubility product was also calculated using a stoichiometric formula of  $Zr(OH)_4$  although it is made clear in the paper that this formula is an assumption. Huang *et al* [8] investigated the differences between zirconium hydroxide ( $Zr(OH)_4 \cdot nH_2O$ ) and hydrous zirconia ( $ZrO_2 \cdot nH_2O$ ) but did not investigate the previously suggested structure  $ZrO(OH)_2$  [9, 10] [11] [12] [13].

The nature of zirconium hydroxide species precipitated under acidic conditions have also been investigated using thermal and x-ray techniques [14, 15]. The suggested structure, which differs from the previous literature, is  $Zr_4O_3(OH)_{10} \cdot 6H_2O$ . The authors compare this structure with  $\alpha$ - $Zr_4(OH)_{16}$ ,  $\beta$ - $Zr_4O_2(OH)_{12}$  and  $\gamma$ - $Zr_4O(OH)_8$  with the major difference being the coordinated water ([14] and references therein). The suggested structure for hydroxides produced at pH 4 and 3 are the same although no data are shown for the pH 3 sample [14].

Clearfield [16] reviews a number of the papers discussed in [14] and points out that the majority of these authors have neglected the work he completed [4] in their assessments of the polymerisation process that zirconium undergoes. He reiterates that the differences seen in the polymorphs of zirconia after calcination can be related to the speed at which the zirconia is produced, with a slower process leading to a more ordered structure that thus forms the tetragonal polymorph and a faster reaction leading to monoclinic. Whilst not directly linked to the wet chemistry, the polymorphs produced have been reported to be associated with crystallite size, with a transition from tetragonal to monoclinic occurring when crystallites grow above 30 nm [17].

Roosen and Hauser discuss some ways in which agglomeration of precipitates can be influenced, listing nucleation rate and nucleation growth as being important to the strength of the agglomerates formed within the precipitation process [18]. In this case the term agglomerates is used to describe; “a limited arrangement of primary particles, which forms a network of interconnective pores”. The primary particles are held together by adhesion forces which are fully discussed in [19]. The strength of such agglomerates can also be influenced by important precipitation parameters such as temperature, pH, concentration and type of reagents and solvents, sequence of mixing, reaction rate, method of mixing as well as the aging of the precipitates [18] [20].

The authors have reported previously the effects of acidity on the formation of zirconium species and the effect of concentration and counter cations on the particle size of the precipitates [1]. The current work examines in more detail the effects of pH, concentration and agitation upon the zirconium species, precipitate particle size, and various processing parameters, thus concentrating on the variables that are simplest to control from a continuous precipitation plant operational perspective.

## 2. Experimental

Detailed sample preparation method for all solutions are available in the literature [1] [21]. Briefly, solutions were made from zirconyl chloride crystals (supplied by Doral Specialty Chemicals Western Australia) dissolved in milli-q water. Two concentrations, 0.81 and 1.62 M, of zirconyl chloride were used. The zirconyl chloride used had been tested for trace elements by ICP-OES and returned less than detectable results [1]. The sample solutions were aged for 10 days at ambient temperature prior to use, all samples were used within 24 hours of the 10 day aging period.

The agitation rate was measured by determining the Reynolds number which was calculated using the standard formula for impellers [22]

$$R_N = \frac{\rho ND^2}{\mu} \quad (1)$$

where

$\rho$  = density

$\mu$  = viscosity

N = Rotational speed

D = Impeller diameter

The target Reynolds number was 10000, being above the turbulent transition zone, for what is defined below as high agitation and a Reynolds number of 5000 for the low agitation [22].

The precipitation method and particle sizing by Dynamic Light Scattering (DLS) are also detailed in [1]. In summary the zirconyl chloride solution and aqueous ammonia were injected into an agitated vessel in the same plane as the impeller rotation. The solution overflowed into a bath of ethanol, which quenches particle growth. The system was started using milli-q water run into equilibrium using four residence times at which point the bath of ethanol was changed. As discussed previously the ethanol is used as a steric hindrent to quench further particle growth [1].

The precipitate was isolated using a Whatmans 541 125 mm diameter filter paper in Büchner funnel and vacuum flask. 304.8 Torr of vacuum was supplied by a Dynavac ODI diaphragm

vacuum pump. To determine filtration rates 250 mL of suspension was poured into the Büchner funnel and the filtration rate timed. Timing was started when vacuum was applied and was stopped once the fluid was not visible within the cake.

The effect that filtering may have on the particle size distribution was investigated. Samples from the filter cakes of the 0.81 M zirconyl chloride precipitated at both pH 3 and 12 were taken. The cake was re-suspended by adding 5 grams of filter cake to 100 ml of ethanol and agitated using a sonic bath for 3 minutes. The suspension was then tested using DLS.

Diffraction data were obtained using an *in-situ* powder XRD system. Samples were placed on a platinum sample well measuring 20.0 x 7.0 x 0.4 mm. Each sample was hand ground in a mortar and pestle with ethanol and was applied directly onto the Pt sample well as a thick slurry. The X-ray data were obtained using an X-ray diffractometer incorporating an Inel CPS-120 curved, position-sensitive detector. The angular range of the detector is 120 deg 2 $\theta$ , facilitating rapid, simultaneous data accumulation. Data were collected in the reflection mode using Cu K $\alpha$  radiation operated at 35 kV and 30 mA. Datasets of 60 s in duration were collected. The XRD patterns were interpreted with the aid of Jade 6.0.3 analytical software (MDI 2003).

DTA/TGA was conducted using a TA Instruments 2969 SDT V3.0F on filter cake that had been dried in a drying oven for 48 hours at 55 °C.

Raman spectroscopy was similarly undertaken on filter cake that had been dried for 48 hours at 55°C .

Micro-combustion analysis was conducted by Dr Thomas Rodemann of the Vibrational Spectroscopy and Elemental Analysis Central Science Laboratory, University of Tasmania.

Optical microscopy was conducted using a Nikon SMZ 800 microscope with a SPOT insight Colour Model 3.2.0 digital camera with external light. Calibration of sizing was achieved using a Graticules LTD 200x0.01 = 2mm graticule.

TEM imaging was carried out on well dispersed samples of precipitates on carbon film. Washed and dried precipitate from 0.81 M solutions at high agitation for both 3 and 12 pH along with calcined ZrO<sub>2</sub>, were investigated using a JEOL 2011 transmission electron microscope operated at 200kV. Energy dispersive spectra for well separated single crystals

were collected at 500-1500 counts per second for 100 live seconds. Elemental compositions of these crystals using calculated k factors were determined using the thin film method [23, 24].

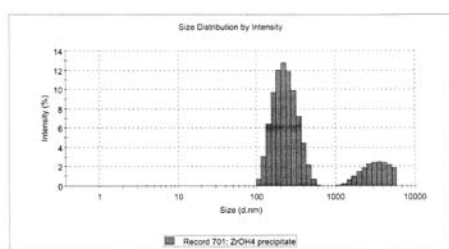
### 3. Results

Table 1 shows the variation of particle size for three variables, pH (3 or 12), zirconyl chloride concentration (0.81 or 1.62M) and agitation (high or low). All three variables were shown to significantly effect the particles size. Increased pH produced smaller particles, increased agitation produced smaller particles and increasing zirconyl chloride concentrations produced larger particles. The largest variation was due to changes of pH. The particle size of the precipitates of zirconium hydroxide produced at pH 12 are one or two orders of magnitude smaller than those produced at pH 3; e.g. using high agitation of 0.81 M solutions, at pH 12 particles were 49 nm compared to 1130 nm at pH 3 (Table 1).

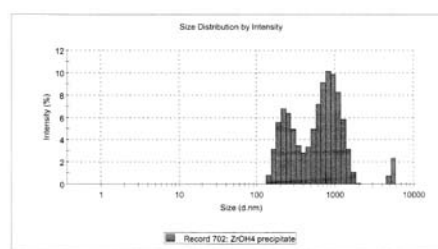
Precipitates produced at pH 12 showed greater variability of particle sizes , e.g. for the 1.62 M solution the difference between the low and high Reynolds number agitation is approximately 10 times (73 vs 743nm). In contrast for the pH 3 sample, the change with agitation for the 0.81 solution is only 1.5 times (1130 vs 1820nm). This could indicate that the particles produced at a higher pH are more prone to mechanical degradation. To test if mechanical degradation was causing the particle size differences the filter cake was redispersed in ethanol using a sonic bath. DLS was used to investigate the PSD of the re-suspended materials (Figure 1). The results indicated the pH 12 sample was effected less by the filtration and re-suspension than the sample produced at pH 3, although both had a bimodal distribution. The resuspended pH 12 sample had the majority of the particles distributed in the region of the initial precipitate, although the distribution displayed is broader. This suggests that mechanical degradation is not the major mechanism that produces the smaller particle size for the pH 12 precipitates. We believe the higher availability of base allows a faster rate of precipitation which in turn leads to the production of smaller particles.

Table 1 Particle size and filtration rates for varying pH, concentrations of zirconyl chloride and agitations.

pH	Concentration of starting solutions	Agitation level	PSD (nm)	Filtration rate minutes
3	0.81	Low	1820	6.8
3	0.81	High	1130	7
3	1.62	Low	3390	4.3
3	1.62	High	2160	5.9
12	0.81	Low	309	>20
12	0.81	High	49	>60
12	1.62	Low	743	>15
12	1.62	high	73	> 60



(a)



(b)

Figure 1 Histogram from DLS (intensity vs. Size) of re-suspended filter cake, (a) precipitated at pH 12. (b) precipitated at pH 3.

Increased agitation generally results in smaller particles, and the results described here are consistent with that expectation. The filtration rates showed a strong dependence on particle size, as expected. Precipitates produced at pH 12 would be unusable industrially as the time taken to filter was excessive.

Figure 2 shows optical micrographs of the dried filter cakes obtained from 0.81M high agitation solutions at pH 3 and 12. Solutions precipitated at pH 12 produced fine well divided powders whilst those produced at pH 3 contained large aggregated particles that were difficult to break apart using a mortar and pestle.

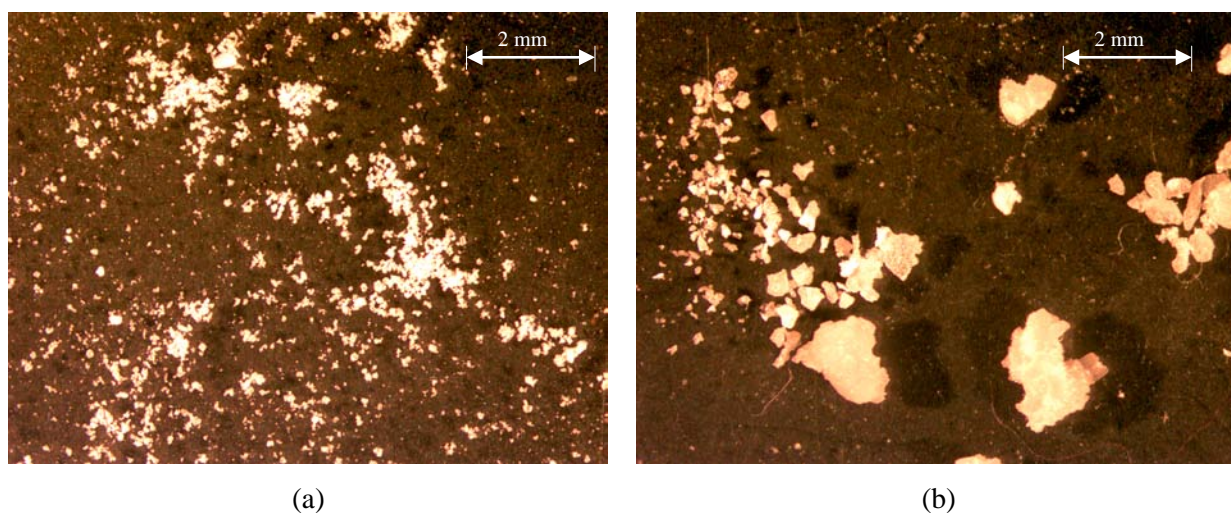


Figure 2 Optical micrograph of 0.81 M dried precipitates (a) precipitated at pH 12. (b) precipitated at pH 3.

The large differences demonstrated suggested the possibility of different zirconia phases being responsible for the varying products. The four high agitation dried precipitates were examined using powder X-Ray Diffraction (XRD) returning a mostly amorphous XRD pattern (Figure 3). A noticeable difference is the peaks seen at 32 and 58 degrees 2 theta for both of the pH 3 samples which are absent in the pH 12 samples. This is due to residual ammoniac ( $\text{NH}_4\text{Cl}$  PDF# 07-007) The peaks observed at 39, 46, 67, 81, 86  $^\circ 2\theta$  are due to the platinum from the sample holder used (PDF# 04-0802).

The presence of ammonium chloride in the samples produced at pH 3, whilst making sense chemically, was counter intuitive in light of the ease with which the filtering and subsequent washing of the filter cake was achieved.

To further investigate the products Raman spectroscopy was carried out (Figure 4) but the patterns returned did not show any changes between either of the starting solution concentrations or the pH's of precipitation. Raman spectroscopy of hydrous-zirconia which was produced by refluxing aqueous zirconyl chloride solutions of differing concentrations has been reported [25]. The data presented show a dependence on solution concentration to the amount of crystallinity determined. The higher concentrations used showed a decreasing tendency to match the spectra given for monoclinic zirconia and thus it was concluded that the material is hydrous zirconia. Huang *et al* [8] discuss at length the differences between hydrous zirconia and zirconium hydroxide and use TGA and XRD to show the differences between the two species.



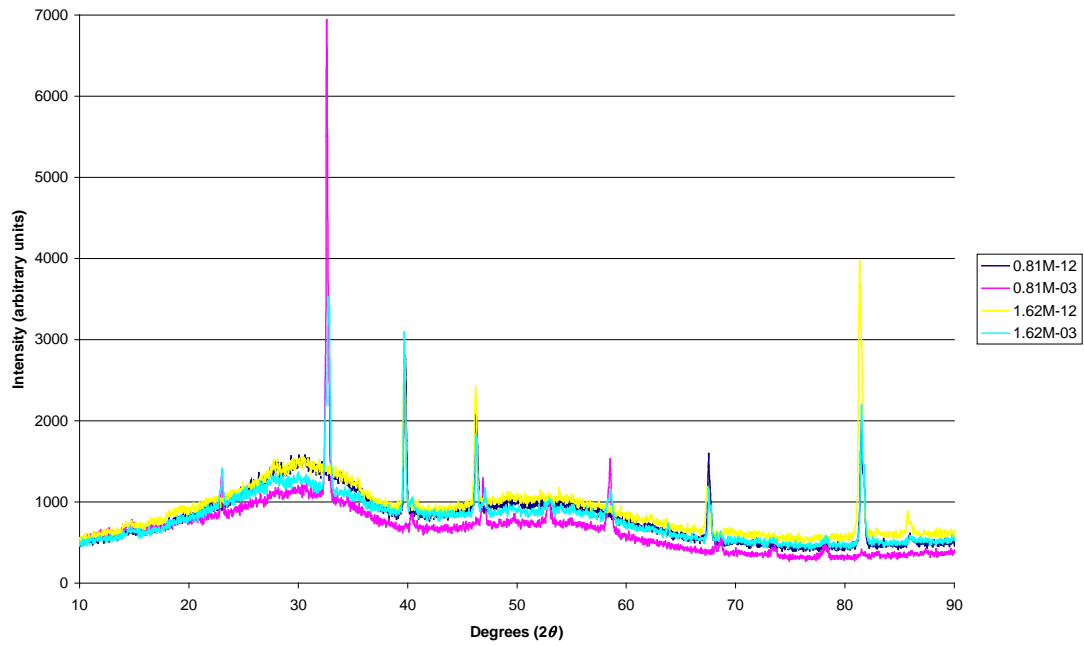


Figure 3 XRD trace of 0.81M, 1.62M, pH3 and 12 precipitated, dried powder showing an amorphous hump (Cu K radiation operated at 35 kV and 30 mA)

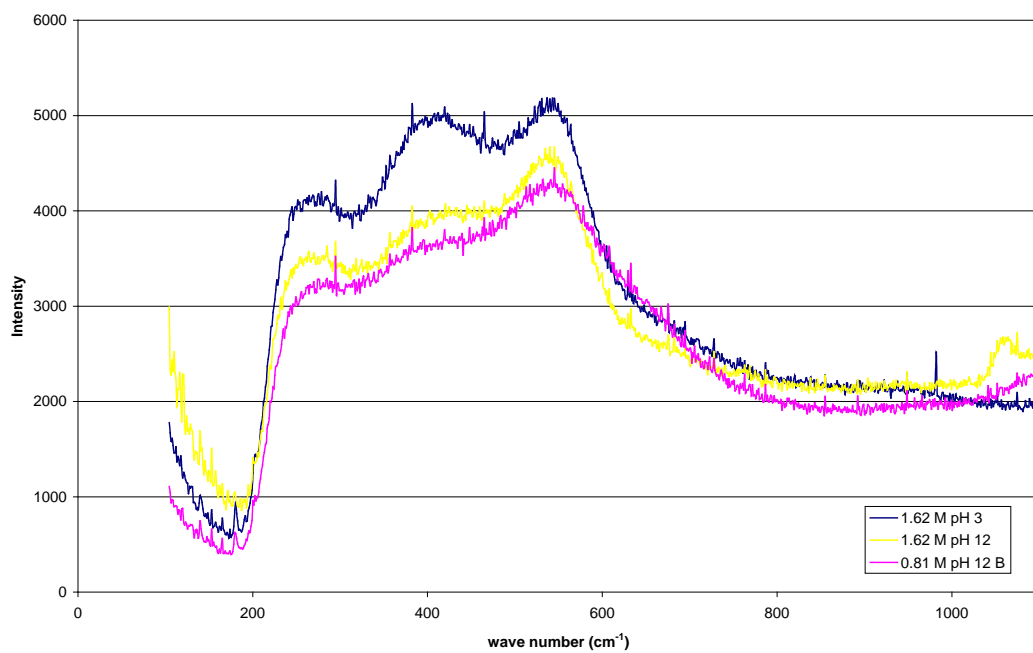


Figure 4 Raman spectra 0.81M, 1.62M, pH12 and a 1.62 M, pH 3 precipitated, dried powder. (Developed using a Dilor Labtram 1B with excitation HeNe - 632.82 nm and a 600 lines/mm diffraction grating)

To investigate the differences in the powder produced by the two different pH values TGA/DTA was conducted (see [Figure 5](#) and [Figure 6](#)). The mass lost for the pH 12 product was 21%, this is in close agreement to the theoretical value of 22.6% for transformation from  $\text{Zr}[\text{OH}]_4$  to  $\text{ZrO}_2$  suggesting that the structure present at a pH 12 may be  $\text{Zr}[\text{OH}]_4$  (see [Figure 6](#)). Rajendran [2] shows three DTA curves where two have smooth single endothermic events the same as seen in [Figure 6](#) whilst the third curve had two separate events similar to that found in [Figure 5](#). The literature explanation was that the two with the smooth endotherms were produced using ethanol and that the ethanol induces the removal of the physisorbed and chemically bound water. The two powders produced using ethanol also had two exotherms reminiscent of the ones seen in [Figure 6](#) with the first occurring around 304 °C being a broad hump with the second being a sharp exotherm. It was suggested that the first broad hump is in all likelihood related to the decomposition of zirconium ethoxide, whilst the second is due to crystallisation [2]. Similar cases can be made in the case of this work however the mass loss from the transformation to  $\text{ZrO}_2$  closely matched the expected value of 22.6% which allows the presence of little else but  $\text{Zr}[\text{OH}]_4$ . The pH 3 precipitated samples that were washed in the same manner as the pH 12 samples had ammonium chloride present as demonstrated by the XRD, as well as water incorporated within the structure along with ethanol if reasoning such as that reported previously was to be used [2].

The presence of these additional components was tested by TGA/DTA with a mass spectrometer attached. Whilst not allowing quantitative analysis, it was expected that distinct points of evolution of water, ethanol and  $\text{CO}_2$  would be found. It was found that ethanol was evolved by both the pH 12 and pH 3 samples as was water and  $\text{CO}_2$ . The points of evolution vary greatly between the pH 12 and pH 3 samples. This then does not allow for the assumption of the structure for the pH 12 to be  $\text{Zr}[\text{OH}]_4$  as no provision is made for the ethanol. However if the alternative ( $\text{ZrO}[\text{OH}]_2$ ) structures is assumed the theoretical change in mass from this to  $\text{ZrO}_2$  is 12.8% and this would thus allow for 8.2% of ethanol. The pH 3 sample had a 32.5% mass loss which allows the starting structure of  $\text{Zr}[\text{OH}]_4$  then as a transformation to  $\text{ZrO}_2$  would leave 9.9% of mass loss unaccounted for which is in reasonable agreement with the difference displayed by the pH 12 sample.

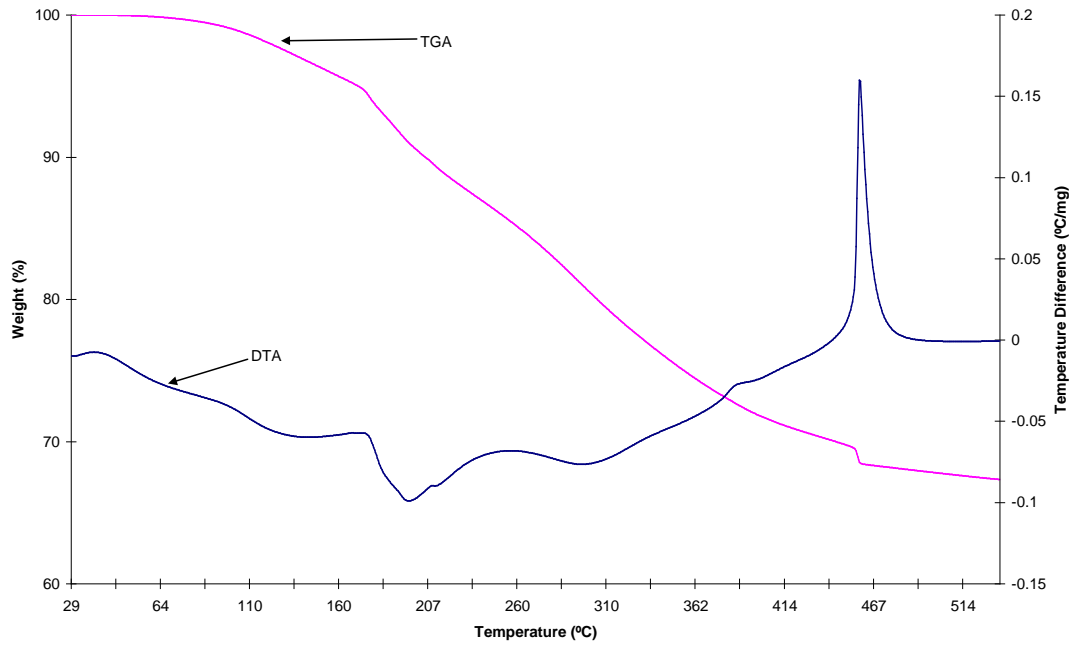


Figure 5 TGA/DTA of 0.81 M solution precipitates pH 3

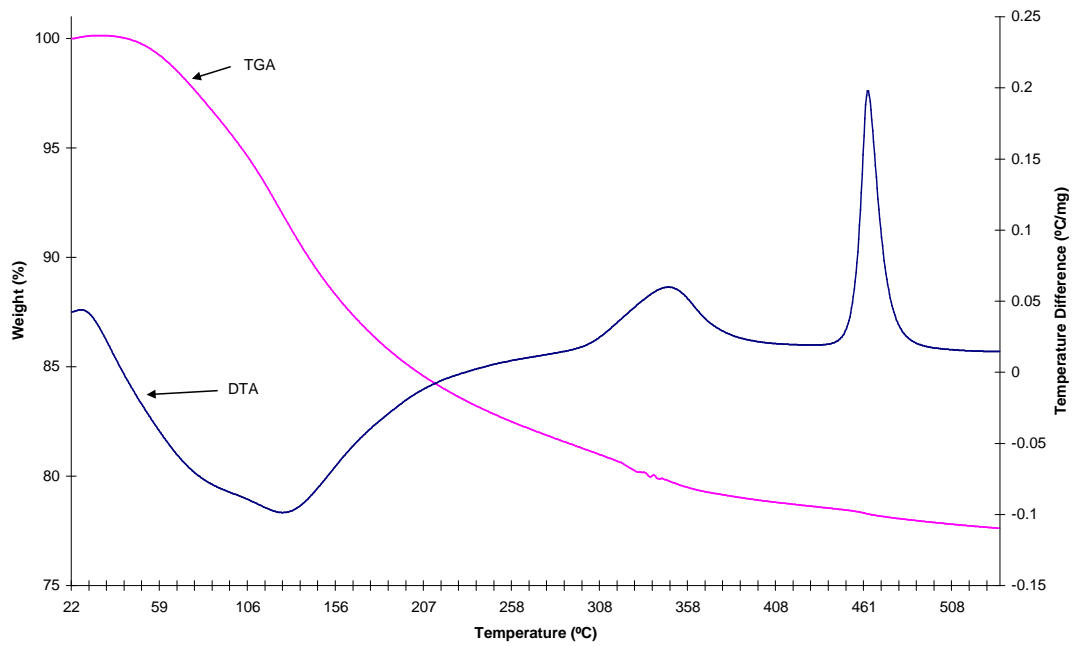


Figure 6 TGA/DTA of 0.81 M solution precipitates pH 12

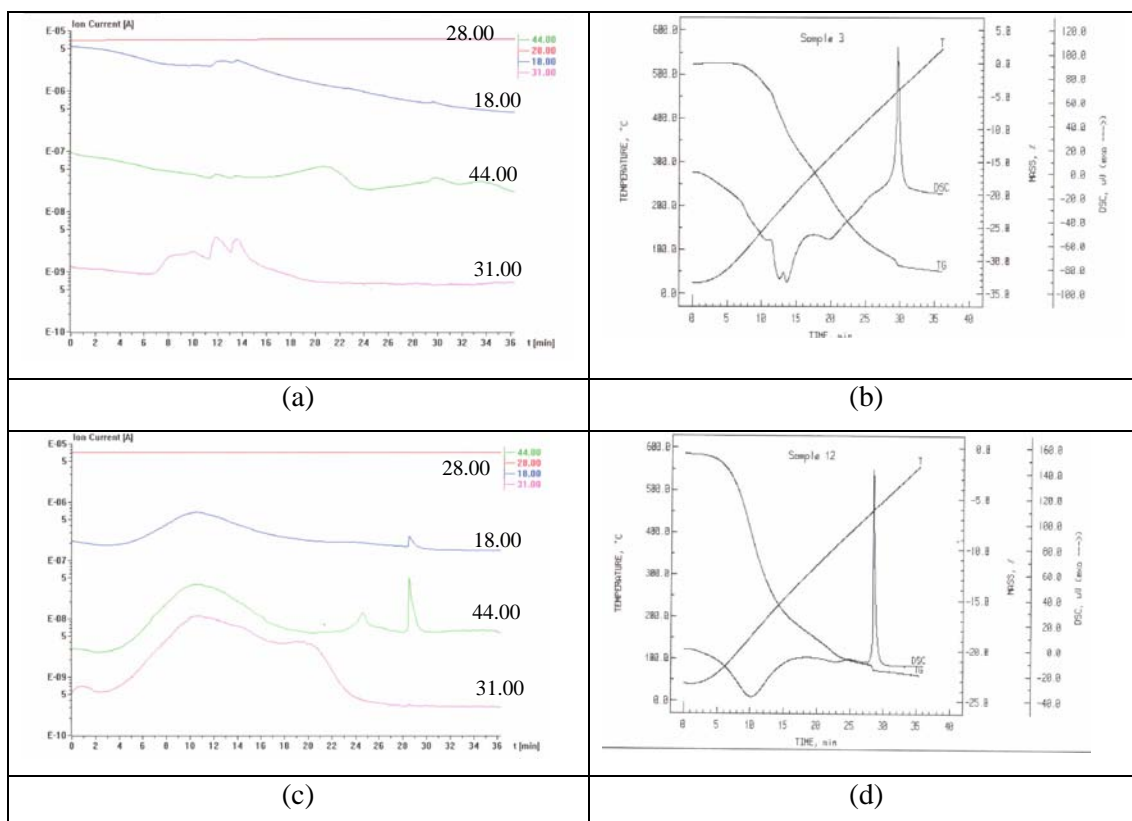


Figure 7 TGA/DTA with Mass Spectrometry, (a) MS output for pH 3 sample (b) TGA/DTA output for pH 3 sample(c) MS output for pH 12 sample (d) TGA/DTA output for pH 12.

To further quantify the products that were being evolved during heating, micro-combustion analysis was performed on the powders produced at a high agitation with a concentration of 0.81 M precipitated at pH 3 and 12 (Table 2). The pH 3 and 12 powders produced had 9.9% and 8.2% mass loss unaccounted for and the values returned in the micro-combustion account well for these masses.

Table 2 Micro-combustion results

element	pH 3 (%)	pH 12 (%)
N	4.52	0.2
C	0.29	3.34
H	2.81	2.40
Total % evolved	7.62	5.94

In the case of the powder produced at pH 3 the micro-combustion results agree well with the XRD results by showing a high nitrogen signature indicating the presence of ammonium chloride whilst the pH 12 show only limited nitrogen and higher C consistent with the presence of ethanol as proposed previously [2].

Elinson and Petrov [11] found that zirconium hydroxides produced from strong hot acidic solution ( $> 1N$  HCl) have the structure of  $Zr(OH)_4$  whilst those produced in weakly acidic solutions were chiefly  $ZrO(OH)_2$ . This is in agreement with the structures proposed above. Guo *et al* [14] alternatively proposed that the structure of zirconium hydroxide produced in acid is  $Zr_4O_3(OH)_{10} \cdot 6H_2O$ . They show TGA/DTA curves for gels produced at pH 4 to justify this structure. These TGA/DTA curves are very different from those produced during this work with one possible explanation being experimental differences.

As the structures proposed to be produced at pH 3 ( $Zr(OH)_4$ ) and 12 ( $ZrO(OH)_2$ ) contain different oxygen to zirconium ratios, samples of each were investigated for the O wt% using TEM EDS. The O wt% returned by EDS for both the pH 3 and 12 precipitated powders as well as a sample of monoclinic zirconium powder (supplied by Millennium Specialty Chemical Rockingham 2003 Z0.5) are shown in Figure 8.

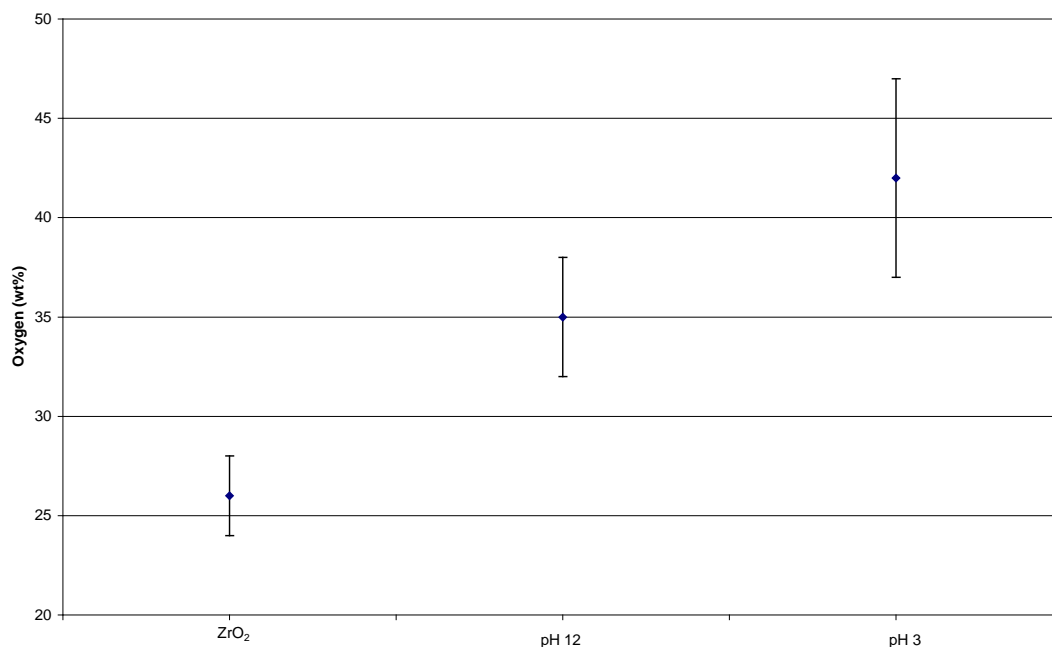


Figure 8 Oxygen wt% from TEM EDS for pH 3, and 12 produced powders as well as a monoclinic zirconia sample.

Although EDS spectroscopy is not an ideal technique for quantitative determination of light elements the authors have successfully used this method to determine Al:O ratios in wear debris from alumina ceramics [26].  $ZrO_2$  has 26 wt% O which is in close agreement with the monoclinic sample tested; this result validates the method used in relation to these samples. Twenty particles of each material were examined. Whilst within the limits of the experimentation it is difficult to distinguish the amount of oxygen present in the two precipitated samples due to the uncertainties, a trend was evident, with the pH 3 sample having a higher wt% O than the pH 12 sample. This result supports the premises that the precipitation conducted at pH 3 results in the formation of  $Zr[OH]_4$  whilst the pH 12 precipitation results in a structure most like  $ZrO[OH]_2$  as suggested by TGA/DTA and micro-combustion work.

The use of the TEM was made particularly difficult by the samples undergoing transformation due to the high vacuum and beam current. This was particularly evident in the powder produced at pH 3, (see Figure 9) all care was taken to exclude such samples from the statistical analysis used in the EDS. It was however possible to take 3 EDS results from the same pH 3 produced sample one after the other without shifting the beam and obtain decreasing values of wt% O for each collection period with the last collection period resulting in a transformation of the sample. Typical values were 45 wt% O on the first collection 35 wt% O on the second and 29 wt% O on the last. This transformation added to the spread of the results and the subsequent increase in the uncertainty's, in addition these values are normalised for Zr and O and do not take into account any H.

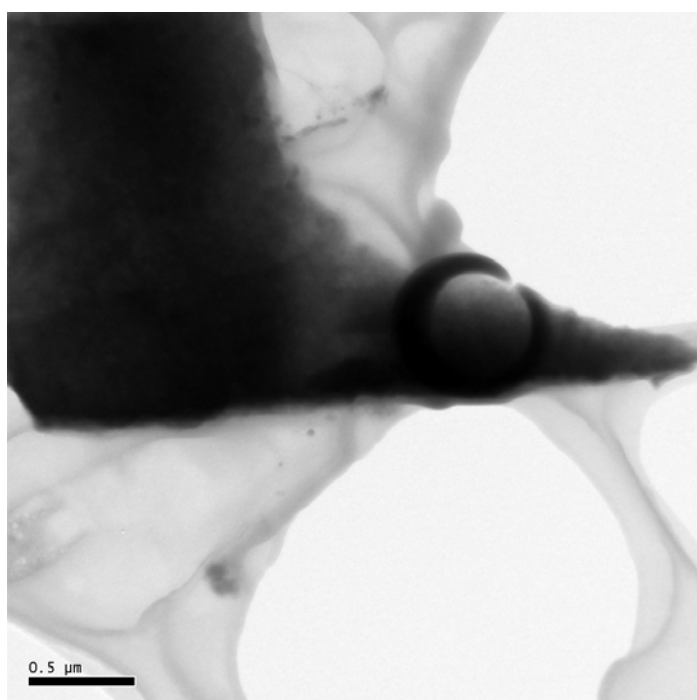


Figure 9 TEM micrograph of pH 3 powder after transformation in TEM

Apart from supporting the structural differences suggested, the TEM work also showed the significant morphological difference in the powders as suggested by the PSD differences and the ability to re-suspend the filter cake. Figure 10 (a) shows a typical particle of the pH 3 powder that has little evidence of being a loose agglomeration; it is more reminiscent of a well compacted cake. In contrast Figure 10 (b) is typical of the pH 12 precipitated powder that has the appearance of a loose aggregation of fine sub particles.

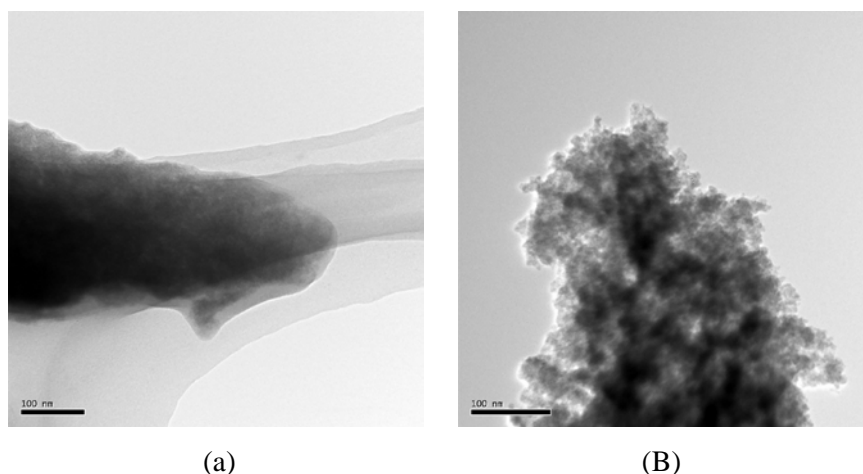


Figure 10 TEM Micrograph of (a) pH 3 powder and (b) of pH 12 powder

## 4. Conclusions

Concentration of starting solutions, agitation levels and the pH that the precipitation is conducted at all effect the particle size distribution for the hydrous zirconium that is produced. The largest change is due to pH with the smallest change occurring when comparing a pH 12 sample with low agitation and a starting concentration of 1.62 M (PS of 743 nm) with a pH 3 sample with the other processing parameters remaining the same (3390 nm); this is an increase by 4.5 times. The largest change occurred when comparing a pH 12 precipitation with high agitation and 1.62 M solution concentration (PS 73 nm) with the same processing parameters except for the precipitation being carried out at pH 3 (2160 nm) which is an increase of greater than 29 times. The effect of the pH of precipitation is most remarkable in that it overshadows all of the other processing parameters with the PS being smaller by 1 to 2 orders of magnitude for those samples precipitated at a pH 12 in comparison to those produced at pH 3. From an industrial processing perspective, the small PS of the

precipitate at pH 12 (743 to 49 nm dependent on processing parameters) leads to significant difficulty in filtering which is an important issue.

An order of magnitude change in PS is not limited to pH changes however as within those precipitations tests carried out at pH 12 changes in the level of agitation also produced order of magnitude differences. The higher agitation in all cases produced smaller PS. As expected lower solutions concentrations were found to produce smaller PS.

The differences seen in the filtering and subsequent differences in morphology of the dried powders, was investigated initially using XRD which showed that those powders produced at pH 3 had retained greater amounts of ammonium chloride. To further investigate the composition of the precipitates TGA/DTA and TGA-MS along with micro-combustion analysis were used with the results suggesting that the pH of precipitation causes differences in the structure of the hydrated zirconium. The pH 3 powders are thought to have a structure most closely resembling  $Zr(OH)_4$  whilst those produced at pH 12 are consistent with a formulation of  $ZrO(OH)_2$ .

TEM with EDS was used to investigate the zirconium to oxygen content of powders produced at both pH values as well as a zirconia sample. It was found that the pH 3 sample had almost 43 wt% O while the pH 12 sample had approximately 32 wt% O. The difficulty in using TEM EDS for light elements precludes detailed analysis but the results returned are in accordance with the different degrees of hydration suggested by the TGA/DTA, and micro-combustion work. The effect that the differing degrees of hydration has on the ceramic process further down stream in the manufacturing process is unclear.

It makes some sense, however, in operational situations to use lower pH precipitation as this will have the double benefit of allowing for lower base input with associated cost reduction and the PS that allows for the most economical filtering. The tuning of both solution concentration and agitation may allow for the targeting of specific PS. In all cases, however, the final ceramic properties must be considered. The structural differences and or other differences between the manufacture systems may impact on the final ceramics.

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