Powder Technology 191 (2009) 218–226

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

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

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ARTICLE INFO

Article history:
Received 25 June 2008
Received in revised form 2 October 2008
Accepted 17 October 2008
Available online 8 November 2008

Keywords:
Zirconia
Precipitation
Particle size
Zirconyl chloride

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.

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]. Whilst 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 that 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 $ZrO(OH)_2$ [9–13].

The nature of zirconium hydroxide species precipitated under acidic conditions has 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 α-$Zr_4(OH)_{16}$, β-$Zr_4O_2(OH)_{12}$ and γ-$Zr_4O(OH)_8$ with the major difference being the coordinated water ([14] and references therein). The suggested structure for hydroxides produced at pH 4 and 3 is the same although no data are shown for the pH 3 sample [14].

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doi:10.1016/j.powtec.2008.10.021

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

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 is 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 h of the 10 day aging period.

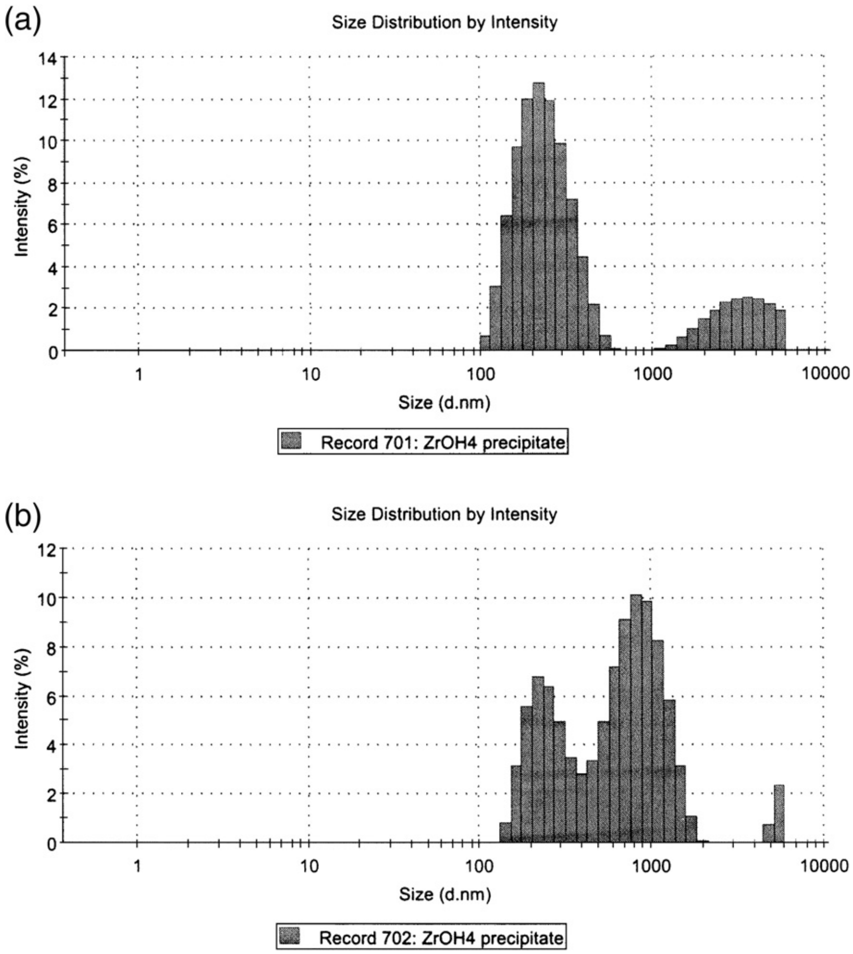

Fig. 1. Histogram from DLS (intensity vs. size) of re-suspended filter cake, (a) precipitated at pH 12. (b) Precipitated at pH 3.