連續式 反應器內에서 熱水作用에 依한 Zirconium Dioxide 의 製造

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Hydrothermal Preparation of Zirconium Dioxide in a Continuous Reactor

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Abstract

A small continuous tubular reactor unit was constructed to study hydrothermal reactions. The unit was used in an experimental research program to study the kinetics of pressure precipitation of zirconium dioxide from aqueous solutions of zirconium tetrachloride. Experimental parameters investigated in the precipitation reaction included the temperature, the reactor residence time, and the feed composition. The significant findings of the study are related to the effect of reaction temperature on the overall rate of precipitation and the effect of feed composition on the precipitation process, which under certain reaction conditions was found to involve an initially slow induction period followed by rapid precipitation. Based on the experimental results, a preliminary design concept was developed for a production-scale unit for manufacturing zirconia having a narrow particle-size distribution.

Introduction

The growing demand for zirconium oxide of high quality, i.e., material with uniform particle size and shape, a high degree of crystallinity and homogeneity and controlled purity, has prompted industry to search for new production processes. A hydrothermal process referred to as pressure precipitation is one such process that appears capable of meeting this demand.

In the production of zirconium oxide by the pressure precipitation process, a solution containing a soluble

zirconium species is heated in a closed vessel, generally an autoclave, for a period of time and at a temperature sufficient to promote hydrolysis of the zirconium species to the corresponding oxide. The oxide is precipitated in a high state of durity (99.9 +percent as noted in *Table* 1), and a high degree of crystallinity and homogeneity, without the addition of precipitants. Many impurities that are precipitated by conventional means such as neutralization, present no problem since they remain in solution.

Table 1. Concentrations of Impurities in ZrO$_2$ Recovered by Conventional Methods and by pressure precipitation[1]

Impurities[a]	Conventional Methods	Pressure Precipitation
Aluminum	0.01–1.0 percent	<20
Iron	4500	50
Magnesium	300	<10
Manganese	30	<5
Nickel	70	10
Lead	25	<10
Silicon	75	95
Tin	<5	<5
Titanium	20	20
Vanadium	<10	<10

a) Analyses on metal basis in ppm except where noted.

The process may be operated batchwise or continuously. In batch operation, the aqueous zirconium solution is sealed in the autoclave and heated to the desired temperature. The resulting slurry is cooled, removed from the autoclave and processed. In continuous processing, the aqueous zirconium solution is pumped continuously through a heated reactor, and the product removed at the other end. Continuous operation as discussed in this article is always preferred because there is no time lost in filling, heating, cooling, and emptying the autoclave as in batch processing. This paper describes the work performed at Battelle's Columbus Laboratories to develop a continuous process for the production of zirconium oxide by pressure precipitation.

Experimental

Construction of Continuous Reactor

A schematic of the continuous hydrothermal reactor is shown in *Fig.* 1. The unit consisted of a feed pump, a tubular reactor, a heat exchanger, and a back-pressure regulator. The unit was designed to operate at temperatures up to 300°C, and pressures up to 1500 psig, with a reactor residence time between 2 and 20 minutes. All wetted parts of the unit were constructed of tantalum and Hastelloy-C to withstand the corrosive environments normally encountered in hydrothermal reactions. Also included in the unit (but not shown in Figure 1) are a pressure feeding device for handling solid-liquid slurry feeds and a turbidity meter for monitoring low concentration (ppm range) of precipitates.
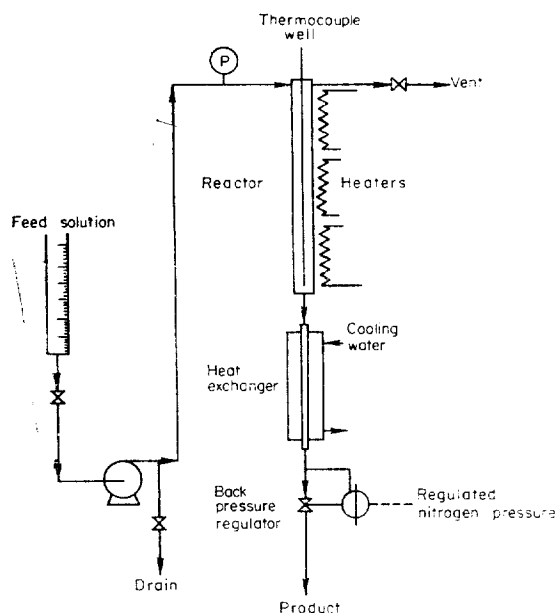

Fig. 1. Schematic of the continuous hydrothermal reactor.

Precipitation of Zirconia in the Continuous Reactor
Experimental Procedure and Results

Precipitation of zirconia from aqueous zirconium tetrachloride solutions was studied using the continuous reactor. The objective of the study was to

investigate the effect on the precipitation process of the following variables:

(1) Temperature between 160 and 180°C

(2) Chloride concentration between 76 and 153g/l on HCl basis

(3) Zirconium concentration in the solution feed between 38 and 80g/l on zirconia basis, and

(4) Residence time (the reactor working volume divided by feed rate) between 5 and 20 minutes.

The effect of the reaction temperature and residence time on the yield of zirconia precipitate is shown in *Fig.* 2. In this series, the yield increased with temperature as expected and essentially reached an equilibrium level of about 96 percent in 10 minutes of residence time at a near-optimum temperature of 180°C for a feed composition of 80.0g/l of ZrO_2 and 76.0g/l of HCl.

The effect of feed composition and residence time on precipitate yield was investigated at a fixed temperature of 180°C. The results as shown in *Fig.* 3 indicate that the acid concentration strongly influences the time required for precipitation to start, which
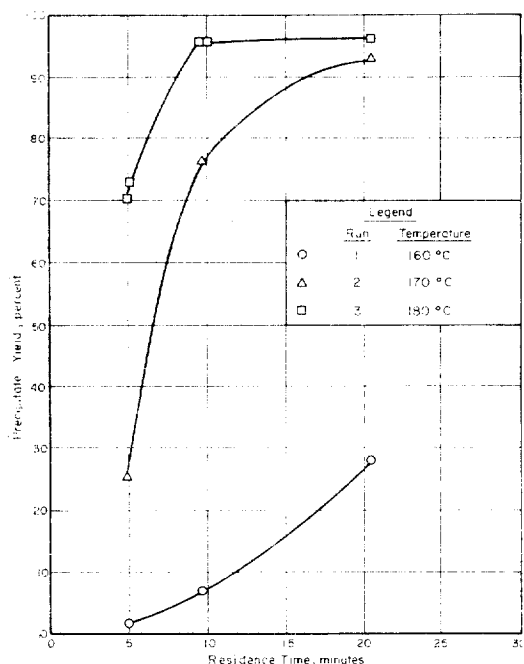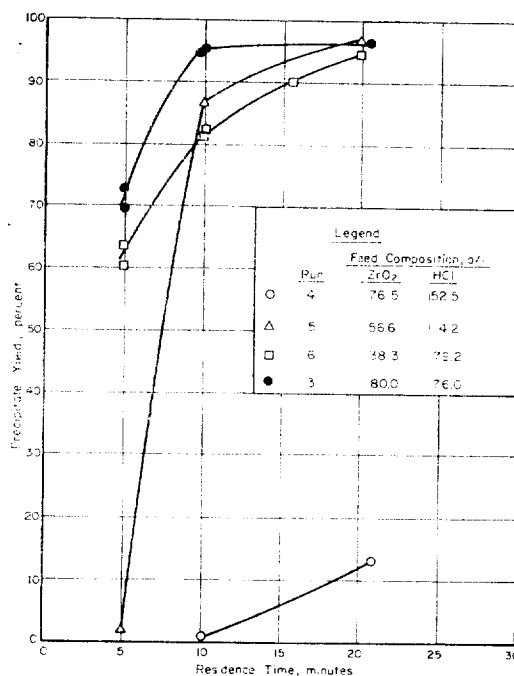

Fig. 3. **Effect of feed composition on zirconia precipitation (Temperature: 180°C).**

for crystallization processes is equivalent to the initial induction period for nucleation. An induction period of 10 minutes at an acid concentration of 152.5g/l (Run 4) decreased to about 5 minutes when the acid concentration was reduced to 114.2g/l (Run 5). At still lower acid concentrations (Runs 3 and 6), the data suggest induction periods to be considerably less than 5 minutes.

To examine the effect of feed composition on the overall rate of precipitation, the data shown in *Fig.* 3 were replotted in *Fig.* 4, showing the concentration of zirconium in solution as a function of residence time. The slope of the curves therefore represents the rate of precipitation. At high acid concentration (Runs 4 and 5) the rate of precipitation was initially low during the induction periods. However, the rate of precipitation was found to increase quite rapidly following the induction period in Run 5. The fast rate of precipitation in Run 5 appeared to persist until the concentration of zirconium in solution was reduced to about 10g/l (ZrO_2), and this rate is comparable to or even higher than the rates for lower

Fig. 2. **Effect of temperature on zirconia precipitation (Feed: Zn as ZrO$_2$=80.0g/l; Cl as HCl=76.0 g/l).**

acid concentrations (Runs 3 and 6).

In Run 4, in which the acid concentration was at the highest level of 152.5g/l (HCl basis), apparently the residence time was not large enough to observe the fast precipitation. Prior work by Stambaugh[1] indicates 96.5 percent yield of zirconia precipitate under feed composition and temperature comparable to Run 4 and a residence time of 15 minutes in a batch-autoclave reactor. Although the continuous and the batch systems are not directly comparable, because of the heat-up and cool-down time involved in batch-system operation, the batch reactor data suggest that precipitation occurs quite readily at acid concentrations comparable to Run 4.

At low acid concentrations (Runs 3 and 6), the data in *Fig.* 4 suggest that initial induction periods were apparently absent or relatively short, and that precitation was more than 50 percent completed within a residence time of 5 minutes. Although the acid concentrations for these two runs were comparable (76.0 and 79.2g/l), the rate of precipitation was higher in Run 3 than in Run 6. The higher precipitation rate was probably due to the higher zirconium

concentration in the feed, which promoted nucleation to occur at a higher frequency with the formation of a larger number of nuclei.[2]

The significant results of the present study may be summarized as follows:

(1) At acid concentrations exceeding about 114g/l (HCl basis), no appreciable precipitation occurs during the initial induction period of 5 to 10 minutes and precipitation proceeds at a rapid rate immediately following the induction period.

(2) At relatively low acid concentrations of around 80g/l, little or no induction period is observed and precipitation occurs at significant rates during the first few minutes of reaction.

(3) The rate of precipitation increases with increasing zirconium concentration in the feed solution.

The significance of these findings related to the problem of reactor design in commercial-scale operation is discussed below.

Application to Large-Scale Processing

Three types of reactor design may be considered for a large-scale operation:

(1) Continuous tubular reactors

(2) Continuous stirred tank reactors (C.S.T.R.), and

(3) Batch reactors.

Large-scale operations favor a continuous type of operation; therefore, one of the two continuous types would be preferred for production-scale reactors. Since a slurry-type reaction system is involved, the problem of keeping the precipitate in suspension would be more easily handled by a C.S.T.R. In view of this important operational problem, a C.S.T.R. appears to be the best system for present application. Additional advantages of the C.S.T.R. include the ease of temperature control and clean up, which are important factors in plant-scale pressure precipitation operations.

The C.S.T.R. is characterized by a relatively broad residence time distribution and by a nearly stepwise change in concentration as the feed enters and mixes with the contents of reactor. In a crystallization
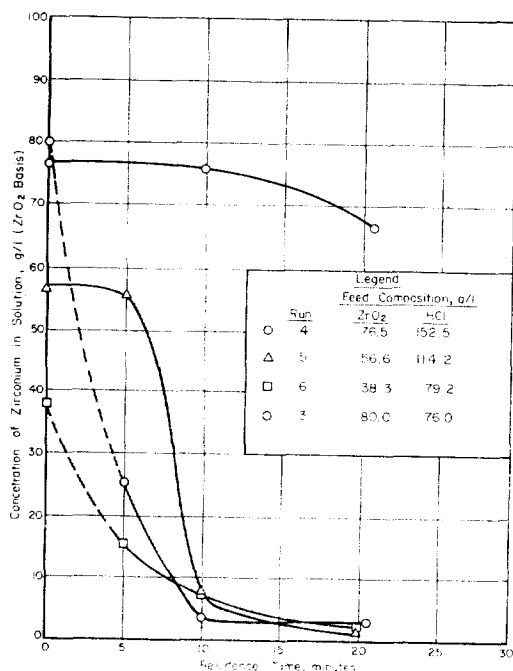

Fig. 4. Effect of feed composition on rate of precipitation (Temperature: 180°C).

process, the broad residence time distribution in stirred-tank operation produces a broader size distribution in the product compared with the corresponding batch crystallization.[3] One consequence of the stepwise change in concentration is that the average reaction rate is lower than it would be in a tubular reactor or a batch reactor, thus requiring a larger reactor volume for a C.S.T.R. operation. To circumvent these problems in a C.S.T.R. operation, a two-step process shown schematically in *Fig.* 5 is recommended for pressure precipitation of zirconia from aqueous zirconium tetrachloride solutions.
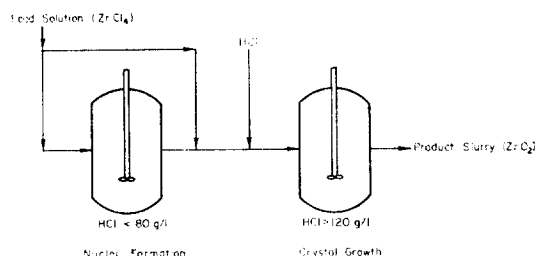

Fig. 5. Schematic of a C.S.T.R. unit for pressure precipitation of zirconia.

The two-step process shown in *Fig.* 5 takes advantage of the precipitation kinetics observed in the present study. The first reactor shown on the left would be operated at a relatively low acid concentration (less than 80g/l, HCl basis) to promote rapid formation of nuclei. The residence time would be kept short (less than 5 minutes) to maintain a high concentration of zirconium in solution in order to maximize the rate of nuclei formation. The effluent from the first reactor would then be fed to the second reactor; the latter would be operated at a relatively high acid concentration (greather than 120g/l, HCl basis) to promote crystal growth and at the same time to suppress formation of additional nuclei.

The residence time in the second reactor would be kept shorter than the induction period corresponding to the acid concentration used to minimize nuclei formation. In this manner, the effect of broad residence time distribution in a C.S.T.R. operation can be counteracted to achieve a more uniform crystal size distribution. Since the rate of crystal growth is high even at a low concentration of zirconium in solution, the stepwise change of zirconium concentration in the second reactor would have little effect on the rate of crystal growth. For example, the concentration in the second reactor could be maintained at around 15g/l (ZrO$_2$ basis) to promote rapid crystal growth and achieve an overall precipitate yield of about 80 percent with an initial concentration of 80 g/l (ZrO$_2$ basis) in the feed solution. The remaining 20 percent of zirconium would be sent with the acid to a leaching step and subsequently recycled to the precipitation process.

References

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