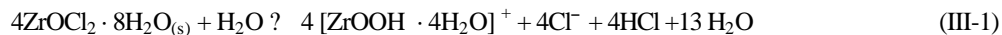


EXPERIMENTAL DESIGN

III-1.0 ZIRCONIUM SULFATE CHEMISTRY

The production of zirconia via the precipitation of zirconium sulfate is fascinating from the standpoint of complex chemistry. The process involves the addition of multiple reactants to achieve the desired stoichiometric ratios of a specific zirconium sulfate product. The chemical reaction chosen to study in this thesis is the precipitation of basic zirconium sulfate, based upon its characteristic agglomeration growth mechanism. One particular polymorph of basic zirconium sulfate is of interest because of its high concentration of zirconium ions per sulfate ion; namely, a hydrated pentazirconyl disulfate (PZDS), $\text{Zr}_6\text{O}_8(\text{SO}_4)_2 \cdot 14\text{-}16 \text{ H}_2\text{O}$ (a molar Zr/SO_4 ratio of 5:2). This precipitated form is defined as a basic sulfate because its Zr/SO_4 ratio is higher than that of the normal zirconium sulfate, $\text{Zr}(\text{SO}_4)_2$ (i.e., 1:2). This acid/base reaction precipitates out this specific zirconium salt, upon the stoichiometric addition of each reactant, at an equilibrium pH of 1.5. The chemical mechanisms for (1) the hydrolysis of the acid reactants and (2) the final overall precipitation have been given much attention in the past, but many aspects still remain a mystery. The explanations and reaction schemes, which follow, are based upon this previous work¹.

The foundation of the solution chemistry for this precipitation reaction is built around one the most widely and best known compounds of zirconium; namely, zirconyl chloride octahydrate, $\text{ZrOCl}_2 \cdot 8 \text{ H}_2\text{O}$ used as feed. In the crystal structure, the dominant zirconium species is in the form of the $[\text{Zr}_4(\text{OH})_8]^{8+}$ ion, with water molecules grouped around this polymeric ion and no cross-linking between the unit zirconium species^{2,3}. When the crystal is added to water, it is readily dissolved and the zirconium polymers are simply lifted out of the lattice into the solution, where they decompose into ZrOOH^+ units. This cationic hydrolysis product is characteristic of zirconium complexes, which are exposed to a chlorine environment. This first hydrolysis step can be written as

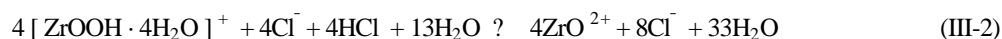


¹ Blumenthal, W.B. (1958), *The Chemical Behavior of Zirconium*, Chapters 3, 4, & 6, D. van Nostrand Co., New York.

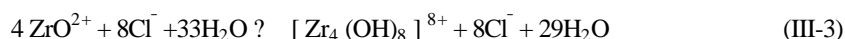
² Clearfield, A. and P.A. Vaughan (1956), *Acta Cryst*, 9, pp. 555-558.

³ Meyer, B.T (1930), *Naturwiss*, 118,34.

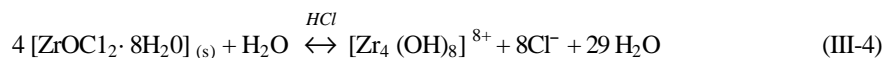
At zirconium concentrations on the order of 0.01 to 1.0 M, this solid is completely dissociated into this stable cation. The physical properties of the zirconyl chloride solution exhibit many of the same characteristics as a solution of hydrochloric acid of the same molarity. The solubility of the total zirconium species in solution can be further controlled by the addition of hydrochloric acid ⁴. This relationship is graphically presented in Figure 1. Upon addition of HCl, the solubility decreases due to the common ion effect, until a minimum at 8.5 N HCl is reached. After this minimum the slight increase in solubility is attributed to the formation of other zirconium complexes. The temperature dependence of the zirconyl chloride solubility ⁵ in concentrated (10.16 N) HCl is given in Figure 2. The role of this noncomplexing acid is more than a solubility control of total zirconium in solution, however; the addition of the chlorine ion into this system is also of equal importance, as we shall see later in this section. The presence of excess hydronium ions forces the previous hydrolysis product on to the next state.



where the further hydrolysis of this metastable hydrous zirconia ion is found to be



It should be reiterated here that the tetramer (in solution) shown in Equation (III-3) would not exist without the addition of HCl. Restated, the complete hydrolysis of the zirconium ion in solution is diminished by the addition of HCl; whereas, the stable ion in the "more basic" aqueous solution is the $[\text{ZrOOH} \cdot 4\text{H}_2\text{O}]^+$ cation. Proof of this tetra-zirconium structure in solution was established using electrochemical techniques ^{6,7} (i.e., the mobility of the zirconium ion in solution for various HCl concentrations up to 1 N). Acidities higher than 1 N yielded no migrating species to the cathode, meaning the formation of larger zirconium species. Recall that this equilibrium species in solution is the same as that in the solid crystalline structure of zirconyl chloride octahydrate in that no chlorine atoms are covalently bonded to the zirconium atoms. The overall hydrolysis (a compilation of Equations (III-1)-(III-3)) of the solid zirconyl chloride can be summarized as



⁴ Hevesy, G. von (1925), Det. Kg. Danske Videnska b. Selskab VI, 7.

⁵ Schmid, P. (1927), Z. anorg. allgem. Chem. 167, 369.

⁶ Braun, W. W., Titanium Alloy Mfg. Div. of the National Lead Co., unpublished researches.

⁷ Lister, B.A.J. and (Miss) L.A.M^cDonald (1952), J. Chem. Soc. 1952, pp. 4315-4330.

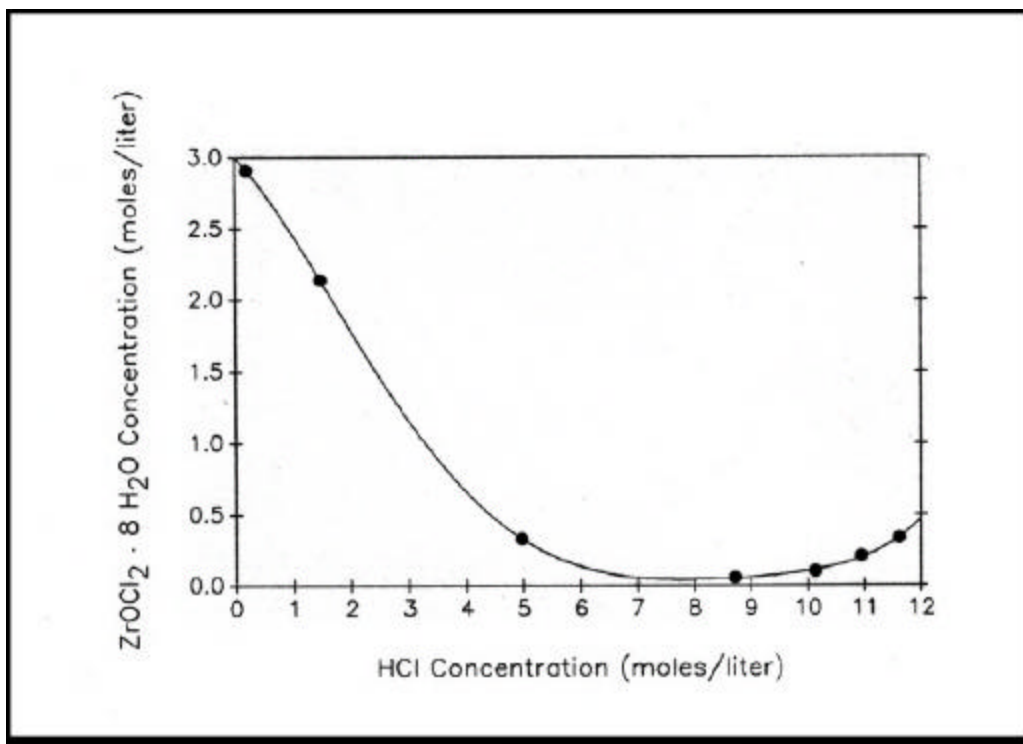


Figure 1: The solubility of zirconyl chloride octahydrate at 20 °C various concentrations of hydrochloric acid. [Redrawn, without permission: Hevesy, G. von (1925), *Det. Kg. Danske Videnska b. Selskab* VI, 7.]

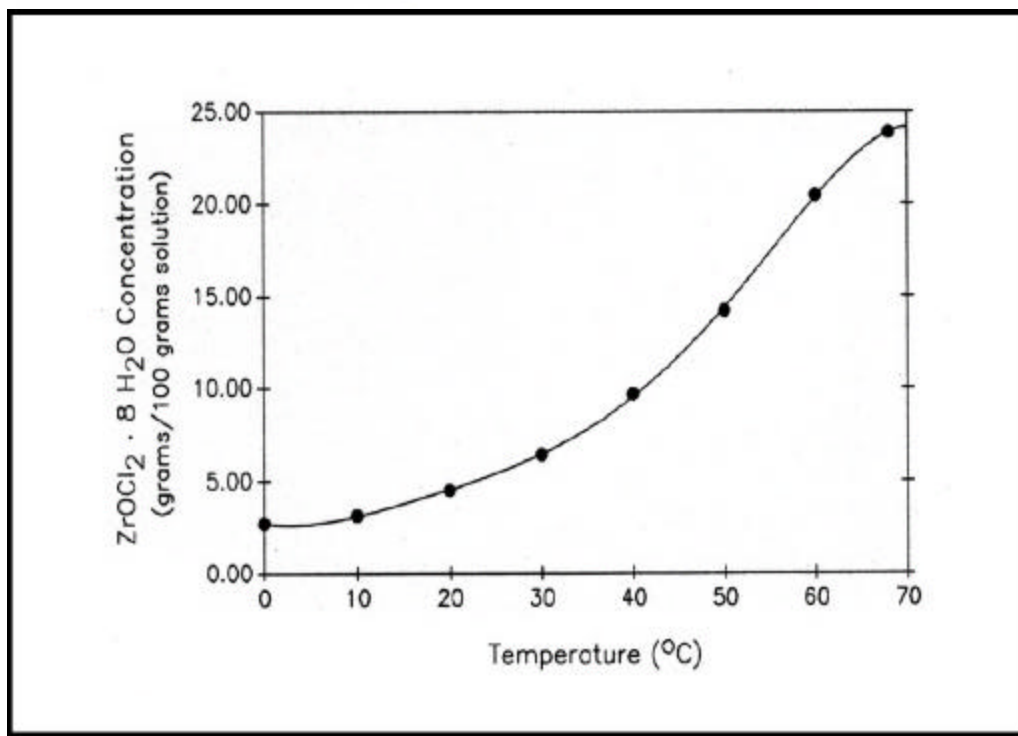


Figure 2: Temperature effect on the solubility of zirconyl chloride octahydrate in 10.16 N hydrochloric acid. [Redrawn, without permission: Schmid, P. (1927), *Z. anorg. allgem. Chem.* 167, 369.]

The dissolution and hydrolysis of zirconyl chloride just presented is a multivariant process. We only presented the steps as they are believed to happen if the temperature, pH, zirconium concentration and hydrochloric acid concentration are at the "correct" levels. These process conditions all have one thing in common; however, and that is they all contribute to the degree of hydrolysis in their own way; which as a result controls the precipitated form of zirconium sulfate. For the hydrolysis of zirconyl chloride, two of these four parameters are further explained by Figure 3, which is generated from the characteristic hydrolysis constants given in Table I.

Table I Formation constants for the hydrolysis of various Zr^{4+} species in aqueous solution at 25 °C. [Reprinted, without permission: Baes, C.F. Jr. and R.E. Mesmer (1976), The Hydrolysis of Cations, p. 158, John Wiley & Sons, New York].

$$\log Q_{XY} = \log K_{XY} + a \left(\frac{\sqrt{I}}{1 + \sqrt{I}} \right) + bm_c$$

Zr^{4+} Species	Log K_{XY}	a	b		
			$m_{ClO_4} = 0.1$	$m_{ClO_4} = 1$	$m_{ClO_4} = 3$
$[ZrOH]^{3+}$	0.3	-3.066	1.4	0.61	0.34
$[Zr(OH)_2]^{2+}$	(-1.7)	-5.111	5.0	1.96	0.95
$[Zr(OH)_3]^+$	(5.1)	-6.132	5.0	1.18	0.73
$[Zr(OH)_4]$	-9.7	-6.132	5.0	1.78	0.68
$[Zr(OH)_5]^-$	-16.0	-5.11	4.6	1.45	0.39
$[Zr_3(OH)_4]^{8+}$	-0.6	10.22	----	(0)	----
$[Zr_3(OH)_5]^{7+}$	3.70	3.066	----	(0)	----
$[Zr_4(OH)_8]^{8+}$	6.0	4.088	----	(0)	----
$ZrO_2 (s)$	-1.9	6.132	-5.0	-1.78	-0.68

* The values in parenthesis are believed to be reasonable estimates of the real values.

In Figure 3(a) we see that as the solution pH decreases below 1.0, the ratio of $[Zr_4(OH)_8]^{8+}$ to other hydrolysis products (e.g., $[Zr_3(OH)_5]^{7+}$) decreases also⁸. This trend is indicative of an increase in hydrolyzing power for that particular pH. In this case, hydrolysis is defined as the attack and attachment of hydroxyl ions to the zirconium ion. Therefore, an increase in hydrolysis means (for a cation of a salt acting as an acid) an increase in the number of hydroxides per zirconium and consequently a reduction in the overall cationic charge. This is just to show that

⁸ Baes, C.F. Jr. and R.E. Mesmer (1976), The Hydrolysis of Cations, p. 159, John Wiley & Sons, New York.

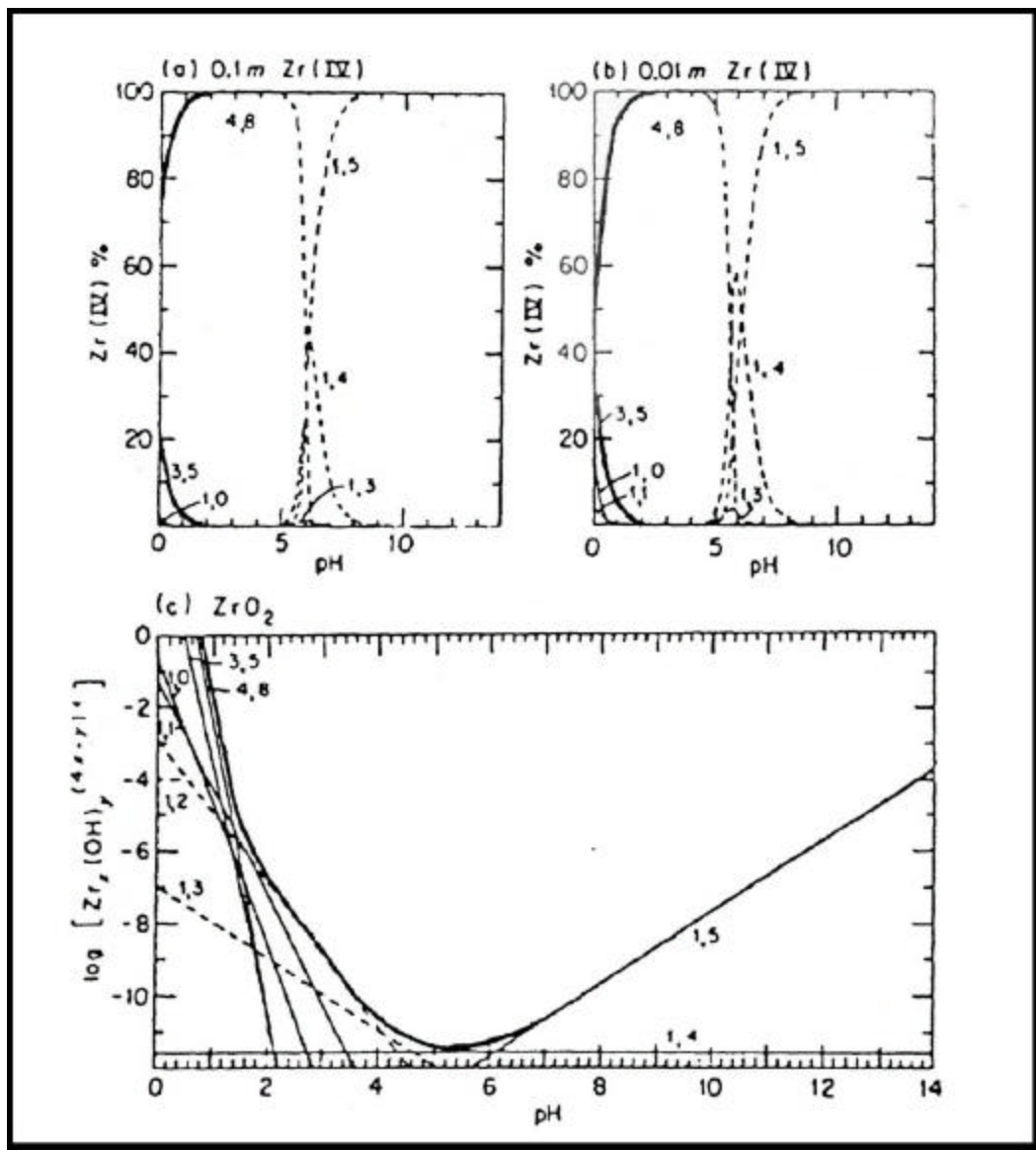


Figure 3: Distribution of hydrolysis products in (a) 0.1 M Zr^{4+} and (b) 0.01 M Zr^{4+} and (c) ZrO_2 saturated solutions. The ionic strength is 1 M at 25 °C. [Redrawn, without permission: Baes, C.F. Jr. and R.E. Mesmer (1976), *The Hydrolysis of Cations*, p. 159, John Wiley & Sons, New York].

different polymorphs of zirconium do exist at differing pH values. Presented in Figure 3(b) is the same relationship as previously seen in Figure 3(a) with the exception of a tenfold decrease in concentration. This dilution effect results in a substantial decrease in the ratio of 4:8 to 3:5 (for example), meaning an increase in the degree of hydrolysis under these conditions. The plot shown in Figure 3(c) describes the total solubility of zirconium in aqueous solution as a function of pH. This relationship reaffirms the fact that the solubility of the zirconium ion increases with increasing acidity, below a pH of 5.5. This key point is, in effect, the same for all the other.

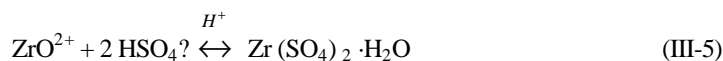
Table II: The qualitative effect of key process variables on the degree of hydrolysis for zirconyl chloride solutions.

Process Variable	Change in Process Variable	Effect on Hydrolysis
pH	?	?
[Zr]	?	?
T	?	?
[HCl]	?	?

process variables. The qualitative influence of the four key processing variables on the degree of hydrolysis is presented in Table II. It should be pointed out that even though the role of HCl is seen to decrease the hydrolyzing power (which has a marketable affect on stabilizing aging effects ⁹) of zirconyl chloride solutions, the common ion effect of the chlorine ion proves to reduce the solubility of zirconium ion in solution (recall Figure 1).

The hydrolysis product, $[\text{ZrOOH} \cdot 4 \text{H}_2\text{O}]^+$, in Reaction (III-I) is considered the monomer unit for this controlled hydrolysis reaction. In fact, as the extent of hydrolysis increases hydrous zirconia sols form in quantitative amounts. In aqueous solutions of zirconyl chloride, large numbers of ZrOOH^+ ions associate loosely to form aggregates equivalent to ionic weights of the order of 8000, as determined by Rayleigh light scattering¹⁰. With the idea of controlling the zirconium ion hydrolysis firmly in place, let's look at some other forms, which the zirconium ion can take on.

In order to form the desired zirconium sulfate complex in solution, the sulfate anion must be put into solution in the right proportions and the right form. The addition of sulfuric acid to the zirconyl chloride solution accomplishes this but also produces an interesting competition between the hydrolyzing sulfate ion and the existing hydroxide ions. In general, it might be stated as an empirical rule that the sulfate ion has no tendency to displace *oxo*, a negligible tendency to displace *hydroxyl*, a strong tendency to displace *aquo*, and an extremely strong tendency to displace *hydronium* ligands from zirconium¹¹. Hence when it is desirable to convert oxygen compounds of zirconium to sulfato compounds, a strongly acidic environment must be employed. Under such conditions all bonds between zirconium and oxygen or hydroxyl can be converted to bonds of sulfate. The following reaction describes such a case.

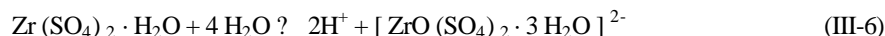


⁹ B-, C.F. Jr. and R.E. Mesmer (1978), The Hydrolysis of Cations, p. 156-157, John Wiley & Sons, New York.

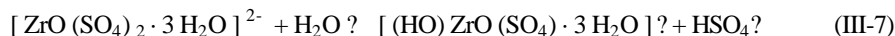
¹⁰ Blumenthal, W .B. (1958), The Chemical Behavior of Zirconium, p. 128, D. van Nostrand Co., New York.

¹¹ Blumenthal, W .B. (1958), The Chemical Behavior of Zirconium, p. 241, D. van Nostrand Co., New York.

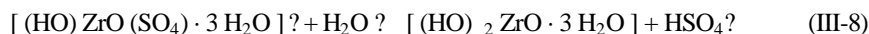
When the acidity is decreased slightly the hydroxyl ions can begin to attack the zirconium ion and to some extent displace the covalently bonded sulfate ions. The result of this first hydrolysis step is an aqueous solution containing a relatively stable transition complex, defined as disulfatozirconic acid trihydrate. This species, shown as the hydrolysis product of Reaction (III-6), is the most common form of the sulfatozirconic acid species.



As can be seen from Equation (III-6), the hydrolysis of sulfate compounds of zirconium produces anions in solution as opposed to the previous hydrolysis of a zirconyl chloride in solution, which produced cations. The monosulfatozirconic ion is also found to exist in equilibrium with the disulfatozirconic ion, shown as



Where upon further hydrolysis yields



Recall, this is the same intermediate (i.e., ZrO^{2+} cation) we saw in Reaction (III-2) in an acidic environment. The tendency for the solubility of the zirconium sulfate complex to decrease as the acid concentration increases is, in fact, the same trend realized before when excess HCl was introduced. From Reaction (III-7) and (III-8) it is seen that as the concentration of excess sulfuric acid increases both reactions are pushed to the left by the common ion effect, thus increasing the presence of the disulfatozirconic acid (the product from Reaction (III-6)). The dependence of the excess sulfuric acid concentration on the zirconium sulfate complex solubility¹² is shown in Figure 4.

The hydrolytic breakdown of the sulfatozirconate structure (meaning covalently bonded sulfate ions) exists by the (1) reduction in chloride ions, in the form of hydrochloric acid (2) increase in temperature (3) decrease in zirconium concentration or (4) by an increase in the solution pH. These four trends are the same as we have seen before for the hydrolysis of zirconyl chloride, with the exception of the solution pH at higher acidities. An increase in acidity is used only when a zirconium sulfate bond is desirable. At lower acidities, slow irreversible hydrolysis

¹² Beyer, C.H., Koerner, E.L. and E.H. Olson (1955), U.S. Atomic Energy Commission Report #ISC-634 (unclassified), "Conversion of Zirconium Sulfates to Anhydrous Zirconium Tetrafluoride".

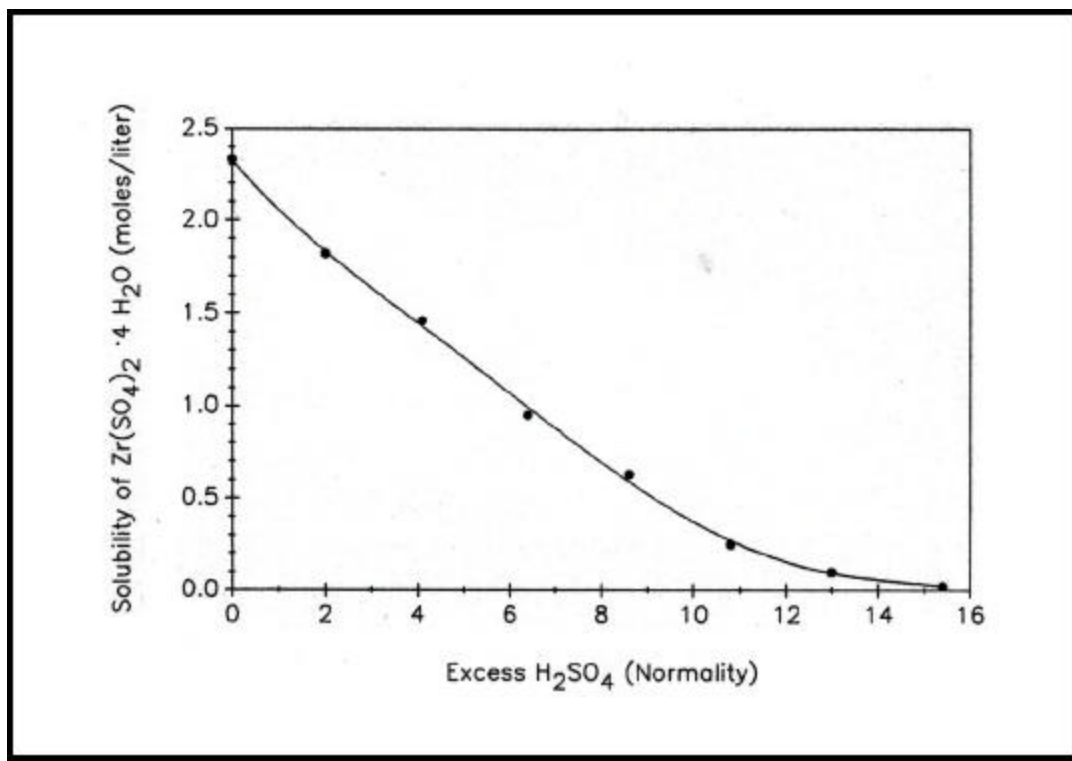
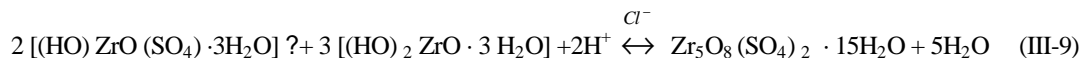


Figure 4: The solubility of normal zirconium sulfate tetrahydrate in various sulfuric acid solutions at 25 °C. [Redrawn, without permission: Beyer, G.H., Koerner, E.L. and E.H. Olson (1955), *U.S. Atomic Energy Commission Report #ISC-634* (unclassified), "Conversion of Zirconium Sulfates to Anhydrous Zirconium Tetrafluoride"].

appears, accompanied by an increase in polymerization and perhaps a change in structure from OH⁻ to O²⁻ bridging¹³. If the conditions are correct such that the hydrolysis is allowed to go to completion, the two transition ions from Reaction (III-7) and (III-8) will combine to give the desired pentazirconium disulfate by



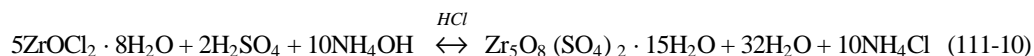
Note here that the pentazirconyl disulfate differs from its intermediates of the sulfatozirconate class in that the sulfate ion; SO₄²⁻ is bonded to the zirconium atom by *electrostatic attraction* rather than covalently¹⁴.

The delicate balance between the zirconium concentration, hydrochloric acid concentration, sulfuric acid concentration, temperature and chlorides content is the main concern in precipitating pentazirconium disulfate. Some of these hydrolysis steps dealing with its formation in solution are quite slow; thus making an equilibrium

¹³ Baes, C.F. Jr. and R.E. Mesmer (1976), *The Hydrolysis of Cations*, p. 156-157, John Wiley & Sons, New York.

¹⁴ Blumenthal, W. B. (1958), *The Chemical Behavior of Zirconium*, p. 271, D. van Nostrand Co., New York.

solution--one that does not change upon standing--somewhat difficult to obtain. Nonetheless, if attention is given to all of the aforementioned principles, the solution chemistry of this ceramic precursor can be controlled. Considering all of the reactions proposed in Equations (III-1)-(III-9), an overall reaction for the precipitation of pentazirconium disulfate can be written as



This proposed reaction scheme was taken as the basis for the production of pentazirconyl disulfate such that reactant concentrations, reaction conditions and design parameters were based upon it. The chemical conditions necessary for this ceramic precursor production were chosen to be

Reactant Temperatures = 25 °C.
 Reaction Temperature, T_r = 80-95 °C.
 Reaction pH = 1.1-1.55.
 Zr/SO₄ ratio in solution¹⁵ = 5/2.
 Zirconyl Chloride Concentration¹⁴, [ZrOCl₂] = 0.2 M.
 Hydrochloric Acid Concentration¹⁴, [HCl] = 1.0 N.

A further discussion of these parameters is given in Section III-3.1.1 of this thesis.

Since rate constants for these hydrolysis steps are not available, it is not really known how long the hydrolysis steps need for completion. For this reason, a so-called "acid feed" (AF) was prepared preceding the start of the precipitation reaction which contained a mixture of the three acids in solution. By mixing the acids beforehand better control of the Zr/SO₄ ratio should result. The next section of this chapter will discuss the logistics of implementing this reaction on a laboratory scale.

III-2.0 REACTOR LAYOUT AND DESIGN OF A CONTINUOUS STIRRED TANK REACTOR.

To achieve the objectives set forth in this thesis, a continuous stirred tank reactor was built around a Mettler Reaction Calorimeter (RCI™ Nänikon-Uster, Switzerland). This Mettler system (as shown in Figure 5(a)) is typically used for batch reaction systems; however, with its adaptable process control software and safety capabilities, this device has been adapted for use with continuous processes. When considering the successful design of any continuous reaction system, the following points should be incorporated¹⁶:

¹⁵ Concentration after mixing all three acids together.

Overall Design Criteria:

- i. The vessel must be small enough so that minimum feed is required, but large enough that sampling does not result in an appreciable disturbance to the system.
- ii. The reactor should be designed so that both the suspension and mother liquor are well mixed--that is, the slurry composition is uniform throughout the volume of the reactor. This perfect mixing condition should be accomplished with a minimum power input so as to minimize particle breakage.
- iii. Slurry discharge should be accomplished so that the discharge suspension density, size distribution, and liquid-liquid composition are the same as in the reactor. There should be no size classification at the discharge point.

III-2.1 RC1™ Unit.

Technical as well as economic considerations are incorporated with the results from the preceding design criteria in order to make a decision on the reactor system as to the size of the experimental reactor and its operating conditions. Once these main operating guidelines are laid out, the specific operating conditions for this unit operation can be established. The purpose of this section is to describe the basis by which the reaction conditions for the continuous processing of zirconium sulfate were decided upon.

Typical laboratory scale precipitators range from 250 ml to 50 liters in size¹⁵. The RC1™ comes equipped with a 2liter jacket reaction vessel (Figure 5(b)) which has automatic temperature control by regulating the circulation of silicon oil through the outer jacket of the reaction vessel, as shown in Figure 5(c). This mid-range reactor is quite adequate for a laboratory scale production facility, such that fluid handling is kept reasonable. The production rate is established once the choice of the mean residence time, t , and reactant concentrations are made. The arbitrary choice of the mean residence time, t , was made based upon reasonable run times when steady state was imposed. Also this choice of t is a function of the specific reaction kinetics associated with each process. For very quick reaction rates it is not necessary to maintain residence times on the order of hours. In fact, Randolph and Larson¹⁷ have shown where longer residence times can often be detrimental to the resultant particle size distribution. Not much is known about the absolute value of the rate constant for this reaction but the kinetics are thought to be generally quick; from this, a mean residence time of 60 minutes was thought to be reasonable. The concentration of the acid feed was fixed at 0.2 M ZrOCl_2 with a molar ratio of Zr/SO_4 of 5/2 and a free acid concentration of 1 N, as previously discussed. This acid feed concentration was held constant throughout all the experiments. Consequently,

¹⁶ Randolph, A.D. and M.A. Larson, Theory of Particulate Processes, 2nd Edition, Academic Press, New York, pp. 239-241 (1988).

¹⁷ Randolph, A.D. and M.A. Larson, Theory of Particulate Processes, 2nd Edition, Academic Press, New York, pp. 215-218 (1988).

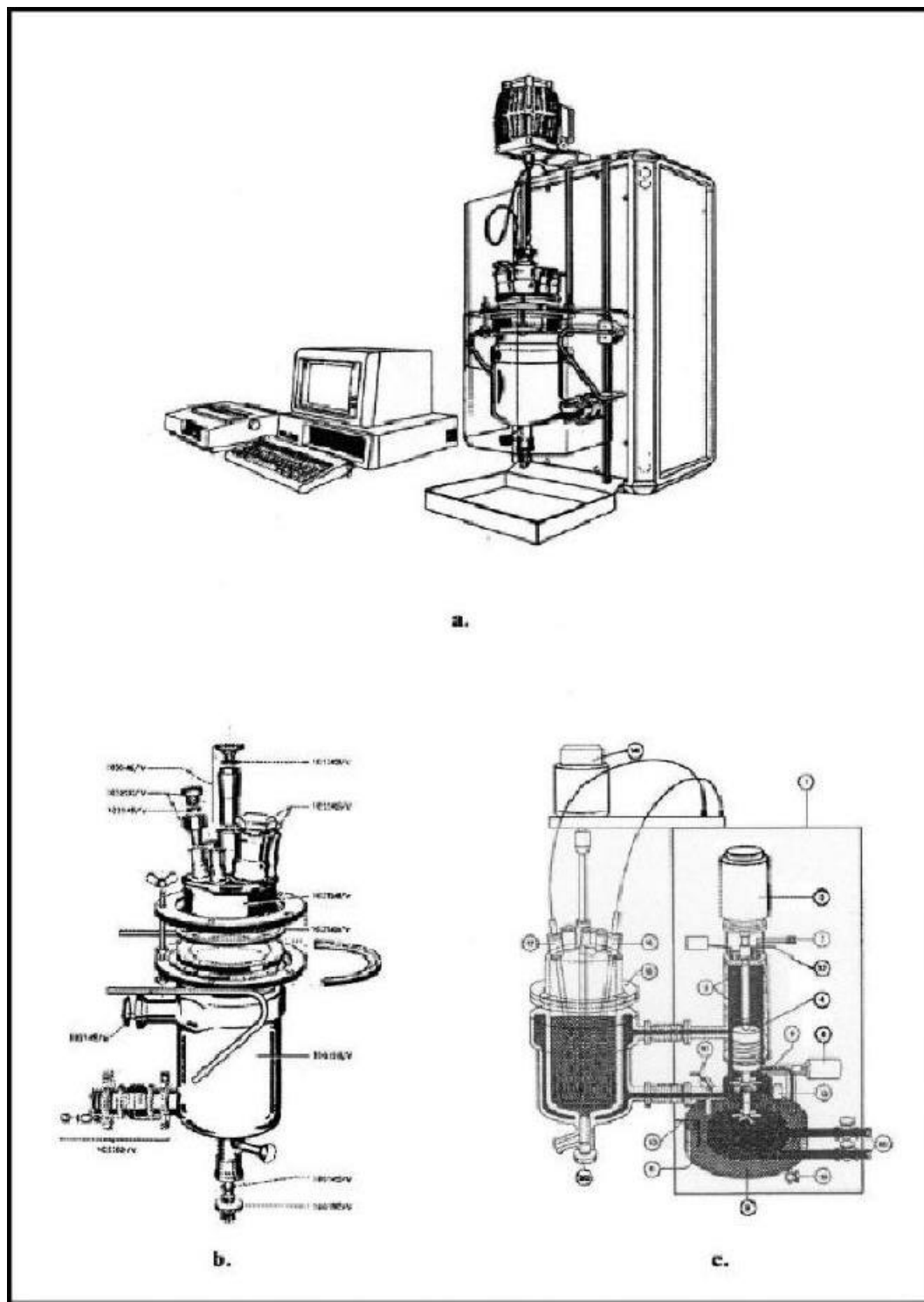


Figure 5: Mettler RC1™ Reaction Calorimeter: (a) RC1™ base unit with computer. (b) schematic of 2-liter jacketed reactor with a L/D ratio of 2.0. (c) reactor heating/cooling system.

the production rate based upon these parameters is approximately 1 g ZrO₂/min, and depends on the base dilution factor .

III-2.2 Reactor Agitation

The successful installation of any continuous stirred tank requires that the vessel be "well mixed". The factors, which determine whether classification exists within the reactor, are multi-variant. A lack of control on the parameters, which control agitation, can result in not only loss of productivity, quality and profit, but can even lead to serious safety incidents¹⁸. Most of these problems can be avoided by careful consideration of the power input per unit volume, reactor geometry and layout before installation. The agitation requirements of a reactor are that not only is a powder suspended uniformly, but that the shear is low enough such that secondary nucleation by particle breakage is minimized. The "just suspended" criterion is sufficient for dissolving solids; however, it is inadequate in attaining homogeneous suspensions with most real systems. A correction for the additional power needed for homogeneity is proposed by Yamazaki *et al*¹⁹. Their empirical corrections yield homogeneous suspension for particles, which have settling velocities less than $1.2 \cdot 10^{-2}$ m/sec. Typical results²⁰ obtained for the precipitation of zirconium sulfate estimate maximum settling velocities on the order of $1.2 \cdot 10^{-2}$ m/sec. The results show that use of the popular Zwietering equation²¹--which is based upon the tip speed necessary for homogeneous suspension--quite often falls short of the minimum power necessary for a constant solids concentration profile. Based upon this empirical correction, estimation to the minimum power necessary was made for our 2-liter reaction vessel, assuming the use of baffles with a hydrofoil stirrer (e.g., see Figure 6(a) and Figure 7, respectively). A value of 1420 RPM's was calculated to be sufficient for this configuration.

An equally important parameter in determining the homogeneity of the suspension is the reactor geometry; which includes the liquid level to the tank diameter ratio (L/D) of the reactor as well as the inserts used to induce turbulence. The "normal" range of the (L/D) ratio goes from 1.0 to 1.5 for many industrial precipitators^{17, 22}. For the reactor shown in Figure 5(b), the (L/D) ratio--when operating at the 2.0-liter volume--is fixed at 2.0. The effect of a larger (L/D) is unclear; however, the key importance is how well the energy is dissipated throughout the reactor. Theoretically, if higher (L/D) ratios are used more attention must be given to the key mixing parameters in order to achieve the same energy distribution as the smaller (L/D) reactor. For this reactor as it stands, if we wish to reduce

¹⁸ Leng, D.E. (1991), Che. Eng. Progress 87, No.6, pp. 23-31, "Succeed at Scale Up".

¹⁹ Yamasaki, H., Tojo, K. and K. Miyanami (1991), Powder Technology 64, pp. 199-206, "Effect of Power Consumption on Solids Concentration Profiles in a Slurry Mixing Tank".

²⁰ Dirksen, J.A. (1988), "Precipitation of Zirconium Sulfate in a Continuous Stirred Tank Reactor, B.S. thesis, University of Utah.

²¹ Zwietering, T.N. (1958), Chem. Eng. Sci. 8, p. 244.

²² Walas, S.M. (1987), Chemical Engineering, March 16, pp. 75-81, "Rules of Thumb".

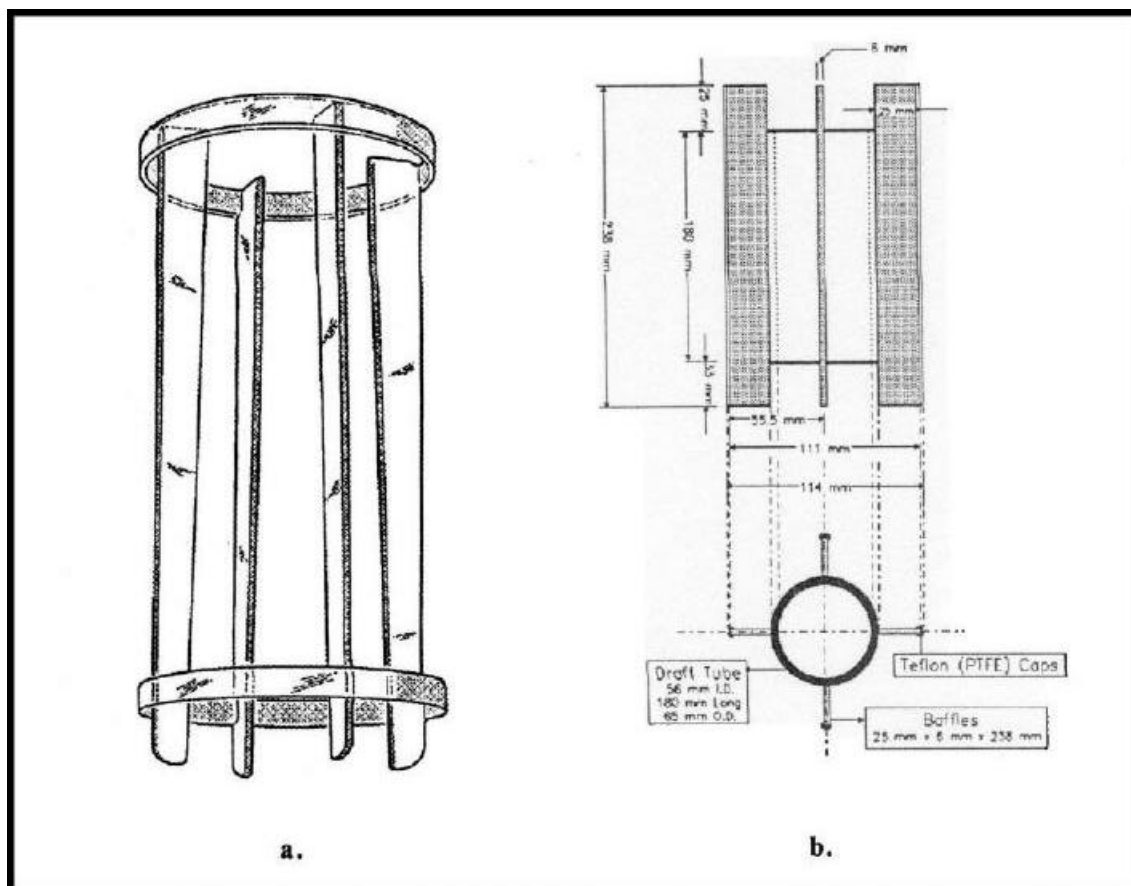


Figure 6: (a) Baffles used in 2-liter RC1™ reaction vessel. Used as purchased from Mettler. The calculated heat capacity for these baffles at 25 °C, is 101 J/K. (b) Draft-Tube design made to fit RC1™ 2-liter reaction vessel. Measured heat capacities and response times are shown in Table II (in Appendix A) as a function of temperature.

the energy input to the system while maintaining uniformity, implementation of a popular configuration^{15,17} called a draft tube, as shown in Figure 6(b), is effective. This device induces turbulence at a lower energy input while also decreasing the nucleation zone; meaning shorter induction times which result in narrower nuclei size distributions. To further assist in this goal, a three-tier hydrofoil stirrer was designed to fit inside the draft tube producing an upward draw. This agitator is schematically presented in Figure 7. By dispersing the energy linearly up the shaft, it is thought to be one way of accounting for the higher than “normal” L/D ratio. Due to the choice in using a draft tube, it is thought that a slightly lower value of the previously determined mixing rate (i.e., 1420 RPM’s) could be used while still maintaining homogeneity. A value of 1300 RPM’s was thought to be sufficient for this purpose.

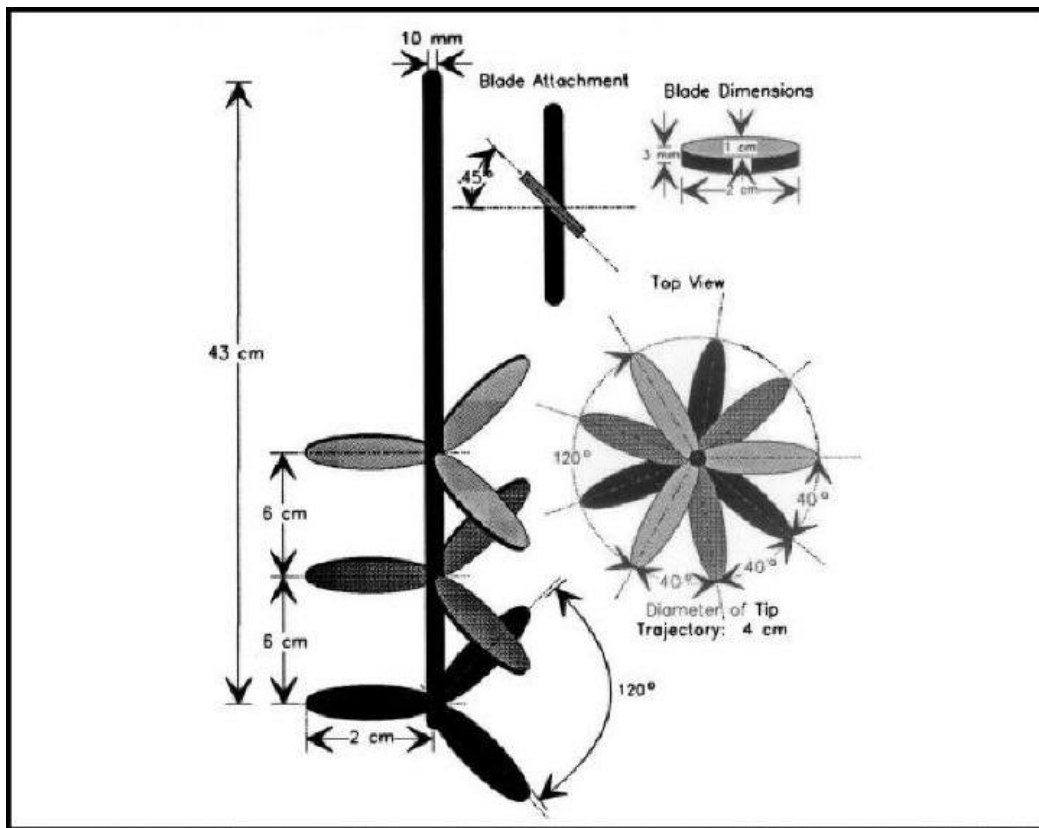


Figure 7: Three-tier hydrofoil used in RC1™ 2-liter reactor. Made for use with draft-tube insert shown in Figure 6(b), but can also be used with baffle insert (Figure 6(a)).

III-2.3 Reactor Layout

If we are to draw any conclusions as to the state of the reactor volume, a reasonable sampling scheme needs to be devised which conforms to the general requirements stated in Section III-2.0. If we are able to extract a representative sample from the reactor volume without disturbing the system, then the well-mixed criterion can be assumed valid. Allen²³ reviews the many sampling schemes for a variety of sampling problems. For continuous processes, the output flow rate must be equal to the input flow rate such that no mass accumulates in the reactor with time. Therefore, by taking advantage of this fact we can devise an overflow line which may also be used as a sample stream at some pulsed frequency. The on/off condition induces a greater chance of drawing representative samples, by close adherence to the "Golden Rules of Sampling"²², which are stated as

Rule 1: A powder should be sampled when in motion.

Rule 2: The whole of the stream of powder should be taken for many short increments of time in preference to part of the stream being taken for the whole of the time.

²³ Allen, T. (1981), Particle Size Measurement, 3rd Edition, pp. 1-35.

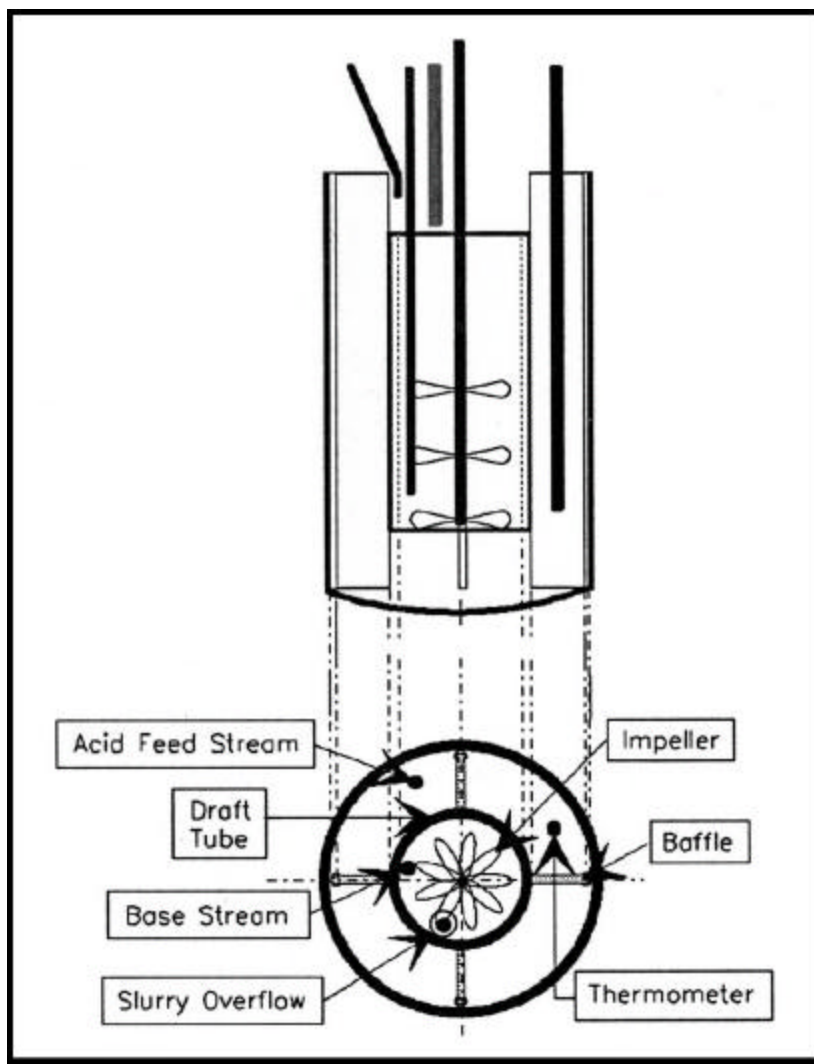


Figure 8: Schematic of 2-liter reactor layout used for the continuous production of zirconium sulfate. With this current layout, the virtual volume of the reactor was 1988 ml at 25 °C, while mixing at 1300 RPM's.

Consideration of these general rules will lead to sampling schemes, which tend to minimize the errors induced by sampling. A schematic representation of the layout of the 2-liter reactor is shown Figure 8, which presents the strategic placement of all the important flow lines and measuring devices. As is shown here the overflow sampling line is isokinetically sampled at the point of maximum fluid velocity in hopes of extracting a representative reactor sample as well as maintaining the no accumulation criterion.

In this figure it is also shown how the acid and base feed stream are injected into the hot reactor volume. The acid feed is injected two-thirds of the way down the reactor on the outside of the draft tube such that a molecule in the acid stream is easily drawn from the bottom up through the circulating draft tube. The base stream enters

above the reactor volume, which allows the base to drop onto the reactor volume at the point of maximum agitation (i.e., the upper lip of the draft tube). The reason for the base stream placement is due to the fact that the base is inducing the precipitation reaction; therefore, the small (3.5 mm ID) glass tube would easily plug up if allowed to be submerged into the liquid.

The upward pitch of the impellers results in a circulating motion up through the draft tube, over the top and down the outside. This scheme would tend to induce less error in sampling; however, if heavy particles are accumulating on the bottom of the reactor a reversal of the motor would force the maximum velocity downward into the reactor bottom thus throwing the bigs up into the main circulating stream. A change in circulation path would constitute a total restructuring of the reactor layout such that sampling adheres to the aforementioned rules and reactant lines are kept free of plugging.

III-2.4 Summary of Overall Design Parameters

The consideration of the previously stated conditions has lead to the successful installation of a continuous stirred tank reactor capable of operating at 0.5 kg ZrO₂/hr. This entire system is shown in Figure 9. The operating procedure for this mini-plant production facility is described in detail in Appendix A of this work. A summary of the important design parameters is compiled in Table III.

Table III: Overall summary of design parameters used in the installation of the 2 liter CSTR facility, shown in Figure 9.

DESIGN PARAMETER	VALUE SELECTED	BASIS
Reactor size	2.0 Liters	RCI Basic Equipment/ Minimum Fluids Handling
Mean Residence Time, τ	60 min.	Run Times/ Reaction Kinetics
Acid Feed Mixture (AFM)	0.2 M ZrOCl ₂ / 0.08 M H ₂ SO ₄ / 1 N HCl	<i>Mixtures' Solubility</i>
Average Production Rate	1 g ZrO ₂ /min.	AFM and τ
Mixing Design	Draft Tube	Nucleation Zone Minimization
Agitator Type	3-Tier Hydrofoil	Attrition Minimization L/D Adjustment
Stirrer Speed, ?	1300 RPM	Minimum Power for Solids Suspension (corrected).
Reactant Pre-heaters	<i>Not Used</i>	Hydrolysis Kinetics
Reaction pH	1.5	PZDS Formation
Reaction Temperature	90 °C	PZDS Formation

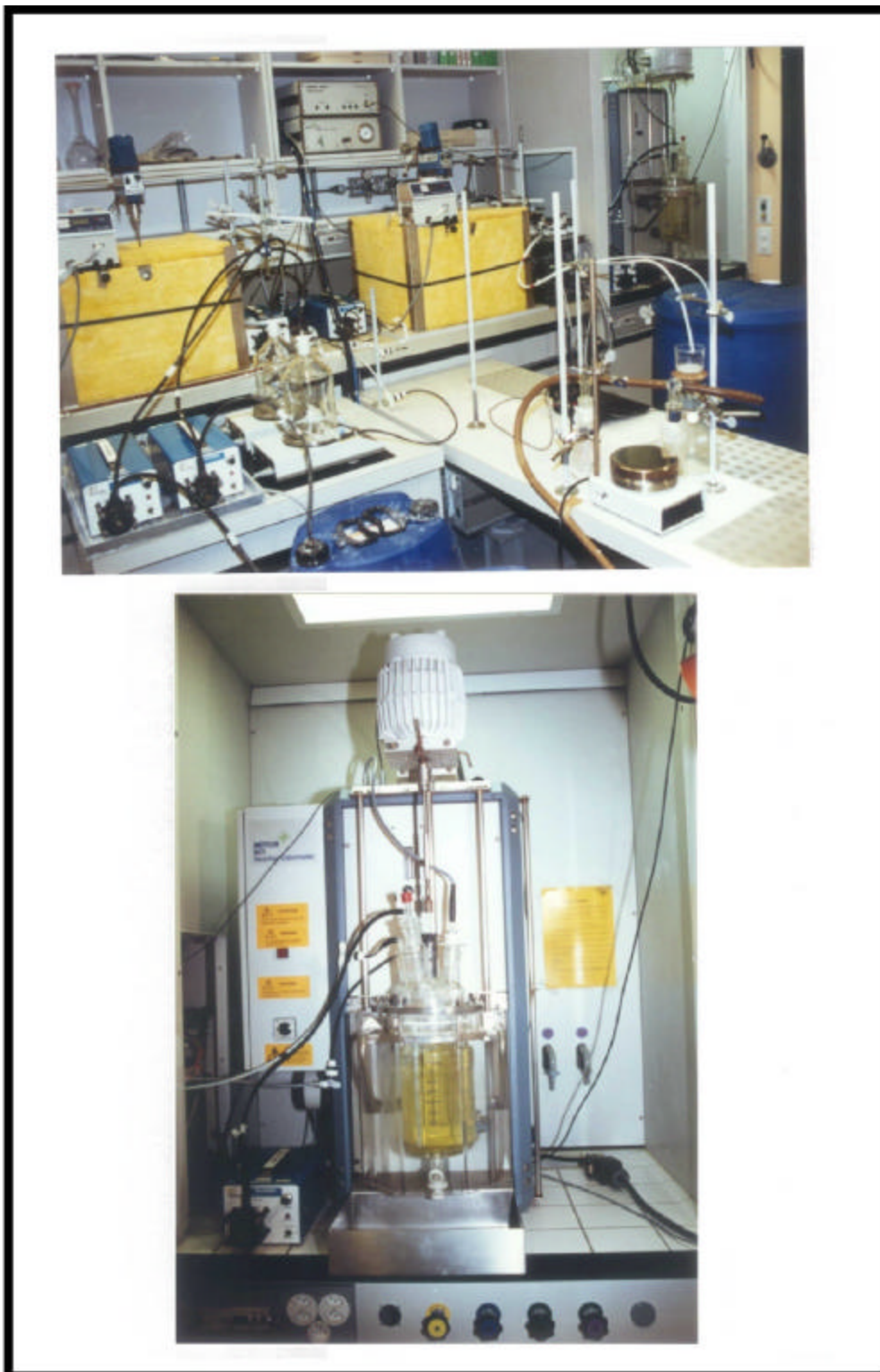


Figure 9: Laboratory scale continuous stirred tank reactor (2-liter reactor) capable of producing 0.5 kg ZrO₂/hr, as installed in the Powder Technology Laboratory at the Swiss Federal Institute of Technology (Lausanne, Switzerland).

The careful planning of experiments, before they are performed, has always been advocated as the norm; however, in the past decade statistics have found their way into this planning stage, which has consequently resulted in a minimization of experiments necessary for the determination of effects. Not only does this efficiency increase, but the inferences which one can draw from the experimental plan are quantified such that confidence levels may be placed on the experimental conclusions. An added bonus to the use of this technique is the ability to see the *interactions* of variables that normally get hidden in the results. The *response variables* were chosen such that a broad overall description could be given to this process. The *response variables* of choice were: (1) Zr/SO₄ ratio (2) number of moles of water adsorbed on the surface (3) an effective void fraction (4) filter rate test (5) specific cake resistance (6) yield (7) impurity levels (8) $\overline{X}_{\text{area}}$ and (9) specific surface area.

The implementation of a partial factorial design was used to determine the effect of six processing parameters on multiple response variables. A two-level factorial design was used which separated the six variables into two separate blocks, ignoring the interactions between the two blocks. These two separate blocks were established by considering that half of the variables were chemically oriented and the other half were engineering oriented. It follows that the two blocks would be defined as the **chemical** and **engineering** blocks.

III-3.1 Experimental Parameter Estimation

The success of any experimental design is extremely sensitive to the choice of not only the variables but also equally the "reasonable" operating range of these variables. For systems that are not previously well studied this task can be somewhat difficult to know the sensitivity of the important factors *a priori*. Consequently, the results of each experimental design are valid *only* for the stated conditions of the design and quite often the trends can be misleading for different ranges of the same variables. For this reason, the choices made in establishing the experiments of this thesis were made based upon an accumulation of results obtained by previous researchers^{1, 11,19,24,25}.

²⁴ Pugh, E.J. (1921), U.S. Patent # 1,376,161, "Process of Making Basic Zirconium Sulfate".

²⁵ Nielsen, R.H. and R.L. Govro (1956), U.S. Department of the Interior: Bureau of Mines Report of Investigations #5214, "Zirconium Purification: Using a Basic Sulfate Precipitation".

III-3.1.1 Chemical Block

The chemical block contains three processing variables, which affect the solubilities, structure and composition of the precipitated powders. The variables of interest are the following:

1. **Base Dilution Factor (DF):** defined as the ratio of the concentrated base concentration, $[\text{NH}_4\text{OH}]_{\text{conc}}$, to the concentration of the base used to induce precipitation, $[\text{NH}_4\text{OH}]_{\text{op}}$, i.e., $\text{DF} = [\text{NH}_4\text{OH}]_{\text{conc}} / [\text{NH}_4\text{OH}]_{\text{op}}$. Detailed descriptions of these starting materials are given in Appendix A.1.
2. **Acid/Base Ratio (R'):** defined as the mass ratio of the acid feed stream to the amount of NH_3 fed, $R' = \text{g Acid Feed} / \text{g NH}_3$. The actual operating parameter for this CSTR is the mass of acid feed to the mass of NH_4OH (defined as R); therefore, the transformation from R' to R is that $R' = R / (\text{wt \% NH}_3 \text{ at operating base concentration})^{26}$.
3. **Reactor Temperature (T_r):** the temperature of the reactor based upon input streams fed at room temperature.

The variability in the dilution factor was based upon the extreme limits possible for reasonable flow rates. A concentrated base was used as the *low* DF (i.e., $\text{DF} = 1$) and a 1.0 M NH_4OH was the concentration of the *high* set point ($\text{DF} = 14.4$, for the base used in this study).

The acid/base ratio, R', theoretically fixes the pH of the reaction mixture if the well mixed criterion is assumed and the reaction kinetics are fast in comparison to the mean residence time. The limits placed on R' were established based upon the conclusions of Nielsen and Govro²⁴ for a batch system under comparable operating conditions. They found that the yield of zirconium is essentially 100 percent in the pH range of 1.3 to 1.6; however, as the pH decreases the solubility of zirconium increases, as shown in Figure 3, thus the yield decreases substantially. The benefit of high acidities, however, is that most metals exhibit the same behavior as the zirconium solubility such that the rejection of impurities increases substantially for the same increase in acidity. Thus an "optimum" pH would be the condition, which produces a powder with the highest purity at the highest yield. They found this range of optimum pH to be from 1.2 to 1.5. Therefore, for the experiments of this thesis we have chosen pH set points of 1.1 and 1.55 as the *low* and *high* values, respectively. For the acid feed concentration chosen, these values of pH correspond to values of R' based upon a titration curve for these conditions. The experimental data shown in Figure 12 (Section III-5.0), fixes these values at $R' = 58.9$ at a pH of 1.1 and $R' = 52.2$ at a pH of 1.55.

The reasonable values of reaction temperature were again selected from batch studies of Nielsen and Govro²⁴. An exponential decrease in filtering times was shown to exist for an increase in temperature (for a temperature range of 70 to 100 °C) with a linear region from 80 to 100 °C. Following from this we have decided upon reactor temperatures of 80 and 95 °C as our respective *low* and *high* values.

²⁶ The concentrated base concentration, $[\text{NH}_4\text{OH}]_{\text{conc}}$, used in this work was 14.4 N (meaning a wt% NH_3 or 27.3%). A diluted base concentration, $[\text{NH}_4\text{OH}]_{\text{dil}}$, of 1.0 N correspond to a wt% or 1.72%.

III-3.1.2 Engineering Block

The other statistical block contains the engineering variables of this study. The effects of this block are not so well established. The engineering block consists of

1. **Mean Residence Time, t :** defined as the total output now rate divided by the reactor volume, $t = Q_T / V_r$.
2. **Mixing Design, MD:** with respect to the types of inserts used. The main reactor configuration was constant but the inserts were changed to study mixing affects.
3. **Mixing Power, MP:** the speed of mixing for the same agitator, as was shown in Figure7.

The choice of an average mean residence time was discussed in Section III-2.1 based upon reasonable run times and the quick reaction kinetics of zirconium sulfate. It is now necessary to determine a sensible variation in this parameter such that changes may be seen in a response variable, if they exist. The change implemented here will be in the direction of longer run times. It is desired to know if in fact the reaction kinetics when performed on a "large" scale is indeed quicker than 60 min. Therefore, the *low* value of t will be set at 60 min. and the *high* value at 120 min.

The variability in the mixing design has already been established also in Section III-2.1. The choice in the two inserts shown in Figure 6, is based upon studying the (1) effect of a different energy distribution in the reactor, for a constant energy input and (2) the effect of decreasing the nucleation zone in the reactor. The choice of low and high variables is based upon the worst and best mixing profiles of the two. Therefore, the *low* condition is given to the baffle insert and the *high* condition to the draft tube.

The study of the mixing intensity on the resultant powder is the purpose of this third variable change. As was shown in Section III-2.2, the estimation of the conditions necessary for the perfect mixing conditions is a difficult one. The values decided upon here are that the *low* mixing intensity be set at 500 RPM's and the *high* value be the previously calculated 1300 RPM's. It is recognized from the outset that the low RPM's should have a larger solids concentration gradient within the reactor making sampling less representative.

III-3.1.3 Block Summary

The final statistical design consists of 16 experiments distributed over two blocks. Each block consists of 8 random variable changes. These experiments were made random to minimize the effect of one run on the following run. This run dependence was also confronted by starting each reaction with a reactor full of 0.06 N HCl solution (a pH of 1.5) such that each production run arrives at its *own* steady state condition. The starting design variables are summarized in Table IV and Table V for the chemical and engineering blocks, respectively.

Table IV: Summary of starting conditions for the statistically designed experiments in the **Chemical Block***.

Run#	Dilution Factor, DF	Acid/Base Ratio, R'	Reactor Temp., T _r
1	1.0	58.9	95
2	1.0	52.2	95
3	14.4	58.9	80
4	1.0	58.9	80
5	14.4	58.9	95
6	14.4	52.2	80
7	14.4	52.2	95
8	1.0	52.2	80

* Constants Engineering Parameters: Residence Time = 60 min.,
Mixing Design = Draft Tube and Mixing Power = 1300 RPM's.

Table V: Summary of starting conditions for the statistically designed experiments in the **Engineering Block***.

Run#	Residence Time (min)	Mixing Design, MD	Mixing Power, MP
1	60	Draft Tube	1300
2	120	Draft Tube	500
3	120	Draft Tube	1300
4	120	Baffle	1300
5	60	Baffle	1300
6	120	Baffle	500
7	60	Draft Tube	500
8	60	Baffle	500

* Constants Chemical Parameters: R' = 54.1, T_r = 95 °C and Dilution Factor = 14.4.

III-3.2 pH Control Stability

The intention of this work is to precipitate zirconium sulfate in a continuous stirred tank reactor while operating at constant conditions over very long periods of time. One key processing variable is the reaction pH. This parameter can affect many facets of the results. The ability to continuously control this parameter is based upon the nature of the systems' response time-- due to mixing, viscosity, reactor geometry, *etc.*--as well as the response time of the particular measuring device. These systematic changes must be accounted for. For this reason, a calibration of the control parameters for a specific system must be determined before any automatic control can be implemented. The dynamic response of our reactor was measured using a method described in Perry's²⁷ as the "Reaction Curve Test". This simple test is applicable to all open loop processes requiring calibration. The process is to induce a process step change and to measure the process response. This characteristic output is enough to estimate the four parameters necessary to stabilize a PID control loop. The four parameters needed for the PID controller are the proportional controller gain, P, integral reset time, I, derivative slope, D, and the process dead time, L. These values were determined for two regions of pH; namely, a pH of 1.0 and 1.6. The results of this test are shown in Table VI.

Table VI: PID pH control parameters for RC1™ 2-liter reactor precipitating zirconium sulfate at 90 °C with an agitation rate of 1000 RPM's using a draft tube insert.

pH	Controller Gain, P	Reset Time, I	Slope, D	Dead Time, L
1.0	75	26	4.0	14
1.6	15	30	5.0	14

The pH controller was used to maintain the reaction pH at a constant value. The success of the control loop depends also on the dependability of the pH probe utilized. Great care was taken in choosing the pH probes for this reaction due to the hostile reaction environment. Measurements at a pH of 1.0 and a temperature of 90 °C for extended periods of time can propose many measurement problems^{28, 29}. The pH probes used in this study were Ingold™ pressurized combination electrodes of type 405-DPAS-K8S. The small internal probe pressure of 0.5 bar

²⁷ Perry's Chemical Engineering Handbook (1984), 6th Edition, p. 22-26, Green, D.W. and J.D. Maloney Editors, M^C-Graw Hi I. New York.

²⁸ Bühler, H. (1980), INGOLD™ Messtechnik, CH-8902 Urdorf /ZH, "pH-Elektroden: Storage, Ageing, Testing and Regeneration".

²⁹ Bühler, H. (1982), INGOLD™ Messtechnik, CH-8902 Urdorf /ZH, "pH-Messung: Principles and Problems of pH Measurement.

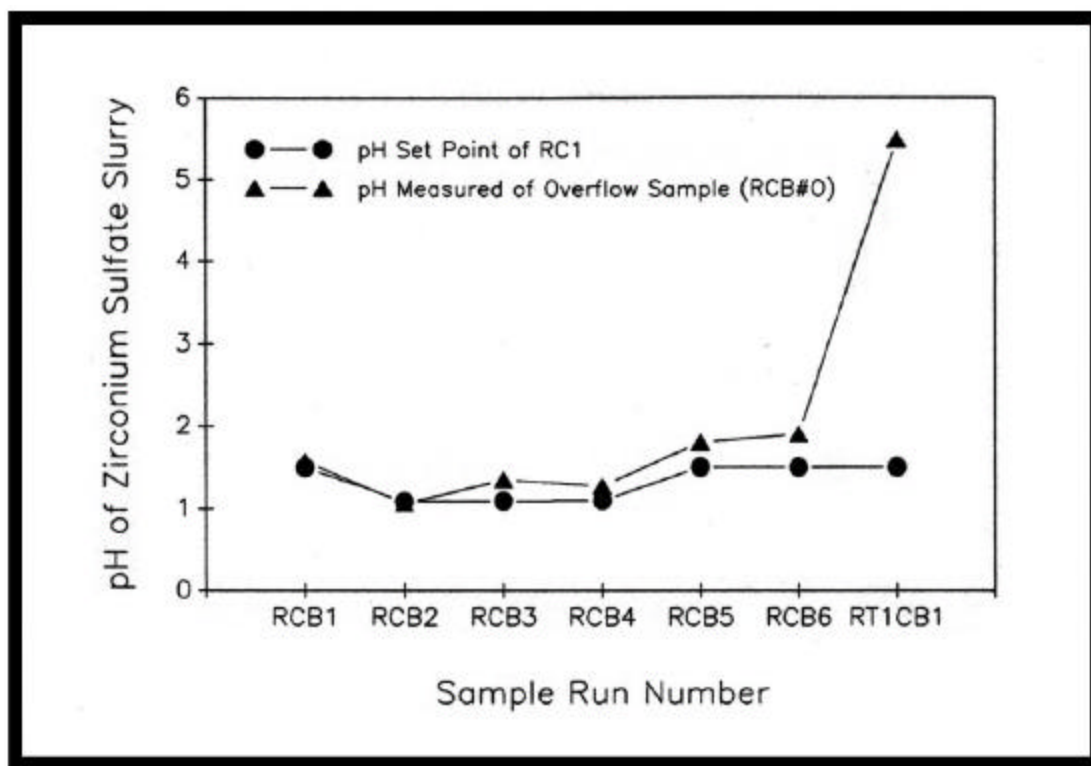


Figure 10: Measured degradation of Ingold™ pressurized pH probes (of type 405-DPAS-K8S, $0 \leq \text{pH} \leq 12$ and $0 \leq T \leq 130$ °C) as a function of production time. Each production run constitutes approximately 8 hours of consecutive run time, for these particular conditions. A new probe was used to start Run #RCB1.

was used to prevent an inward flux of reactants such that particulates form on the membrane. To ensure accuracy in the control loop, the pH probe was calibrated before each run using Ingold™ buffers at a pH of 2.01 and 4.00 at 25 °C with temperature compensation. Watching the changes in the slope and intercept of the pH calibration parameters, one can monitor the degradation of a pH probe. After only a few production runs the slope of a new probe was found to decrease with each calibration. This lead to checking the pH values as measured by the RC1™ (the pH setpoint) versus the values measured of the overflow sample with an external pH, meter calibrated in the same fashion as before. These results are shown in Figure 10 for real production runs. This figure shows how the pH probe degrades with time under the extremely adverse conditions in which this precipitation takes place. It follows, that an approximate lifetime of less than 40 hours exists for these probes under these conditions. This result presents an enormous hazard if we are to be able to accurately control the pH of the reaction over long periods of time. For this reason, an alternative scheme was devised in which constant mass dosing was used for each reactant such that—for a certain ratio of acid to base—there exists a specific reaction pH that is maintained. This scheme was previously presented in Section III- 3.1.1.

III-3.3 Preliminary Pre-Heater Investigation

The fundamental affects of temperature on the "stability" of acidic zirconium solutions- -used in this precipitation reaction--have been previously examined, with similar trends resulting. The hydrolytic temperature affect on zirconyl chloride solutions was demonstrated by heating these acidic solutions in sealed glass capillary tubes to 150 °C; where upon, a solid hydrolysate formed which did not visibly redissolve when the solution was cooled and allowed to stand (although the acid concentration was sufficient to dissolve the ordinary hydrous zirconia)³⁰. The same hydrolytic breakdown was exhibited for zirconium sulfate solutions. These sulfate solutions, at a pH of 2.8, could be heated to 90 °C before precipitation resulted³¹; where solutions with lower pH values than 2.8 would result in higher precipitation temperatures. These zirconium sulfate salts precipitate because of the hydroxylation of the sulfatozirconate ion; where the newly formed hydroxylated species acts as a base with the acid species in the same solution. The characteristic temperature and pH of the hydrolytic precipitation reaction are dependent on the concentrations and proportions of the total acids in solution.

Because of this hydrolytic concentration dependence, it became necessary to establish the characteristic values for the concentrations and proportions involved in this work. The stable "shelf life" of the acid feed (as described in Appendix A) was found to be 3 weeks, before a substantial amount of precipitate formed. If this same mixture is heated to 90 °C, over a period of 15 min., the same hydrolytic breakdown resulted. If the zirconium chloride concentration is increased to 0.3 M (with a 5/2 molar Zr/SO₄ ratio and 0.1 N HCl, added) the precipitation temperature drops to 65 °C. It is apparent that the hydrolytic temperature is extremely sensitive to the "state" of the starting solutions.

To further verify these findings, pre-heaters were installed in both the base and the acids lines such that "hot" reactants (the same temperature as the reactor) could be added on a continuous basis. These pre-heaters consisted of glass coils submerged in hot silicon oil, with the bath temperature controlled by the temperature of the outlet reactant. The glass coils were made from 21 meters of 4 mm I.D./6 mm O.D. tubing, which constitutes a total volume of 0.25 liters. At the average flowrates specified in this work, that suggests residence times on the order of 5 -15 minutes. Pre-heating the acid feed to 90 °C, with these residence times, was found to be sufficient in precipitating out the same hydrolysis product. After 2-3 hours of operation the acid line was completely plugged.

The objective of this work is to present a reproducible, controllable methodology for the preparation of pentazirconyl disulfate on a continuous basis. For this to be possible, the input lines must remain clear of solid seed material otherwise the important formation step must go through a dissolution before a reprecipitation is possible, which presents inherent oscillatory behavior problems in the product removal stream. For this reason, the entire

³⁰ Blumenthal, W.B. (1958), The Chemical Behavior of Zirconium, p. 186, D. van Nostrand Co., New York.

³¹ Hagiwara, Zenji (1953), Technol. Repts. Tôhoku Univ., 17, pp. 70-76.

pre-heating operation was abandoned, and all reactants were fed at room temperature. Pre-heating is possible under certain reactant conditions, however, the "state" of the reactant feed becomes less reproducible. Use of the pre-heaters would also be possible, at reactor temperatures, if separate lines were used for each individual acid stream, where additions and dilutions are made in the reactor itself. However, an inherent homogeneity, and an "off stoichiometry", problem would probably become more apparent. The ability to establish equilibrium in the starting solutions is important if a continuous stirred tank reactor is expected to arrive at a steady state of operation.

III-4.0 DETERMINATION OF REACTOR STEADY STATE

For the effects of various changes in reaction conditions to be quantified, it is necessary to be able to establish what is the "steady state" sample for each process change. When precipitating on a continuous basis this equilibrium state becomes much more difficult to establish. The degree of "homogeneity" in the reaction mixture must first be established before prediction is possible. That is, what is the desired steady state condition? Some response variables are more sensitive than others to changes, which demands a greater accuracy in the final response. In general, this means that more residence times are necessary in establishing this condition. Therefore, the proposed number of residence times necessary to achieve this condition vary from $5 \cdot 10^{21}$ to $10 \cdot 15^{15}$ depending on the choice in response variables, mixing intensities, reactor geometries, rate constants, *etc.* If an ideal continuous stirred tank reactor is assumed--which is defined as a reactor in which fluid enters and leaves solely by plug flow--the time to arrive at steady state is given by Levenspiel³² as the percentage steady state (SS), stated as

$$SS = \left[1 - \exp\left(-\frac{t}{t}\right) \right] 100 \quad (\text{III-11})$$

For example if a 95 percent or steady state is desired then 3 t 's are predicted as sufficient. However, to account for the non-idealality of a particular system, each reactor performance should be measured. A zirconium sulfate production run (#SS2) was monitored just for this purpose. The conditions of this run were the same as those proposed in Table V; Run # 1. It should be noted here that the starting point of each reaction was that the predescribed reactants were added to a 2.0-liter, hot 0.06 M HCl solution (pH=1.5) already present in the reactor. In order to characterize steady state for our system, 4 response variables were monitored with time. These results are given in Figure 11. From this figure it is possible to determine a reasonable steady state condition for our system. For the changes shown in the various response variables, only the response of the filter rate test shows a lower percent of steady state than 95% after t_6 .

³² Levenspiel, O. (1972). Chemical Reaction Engineering, 2nd Edition, pp. 257-264. John Wiley & Sons, New York.

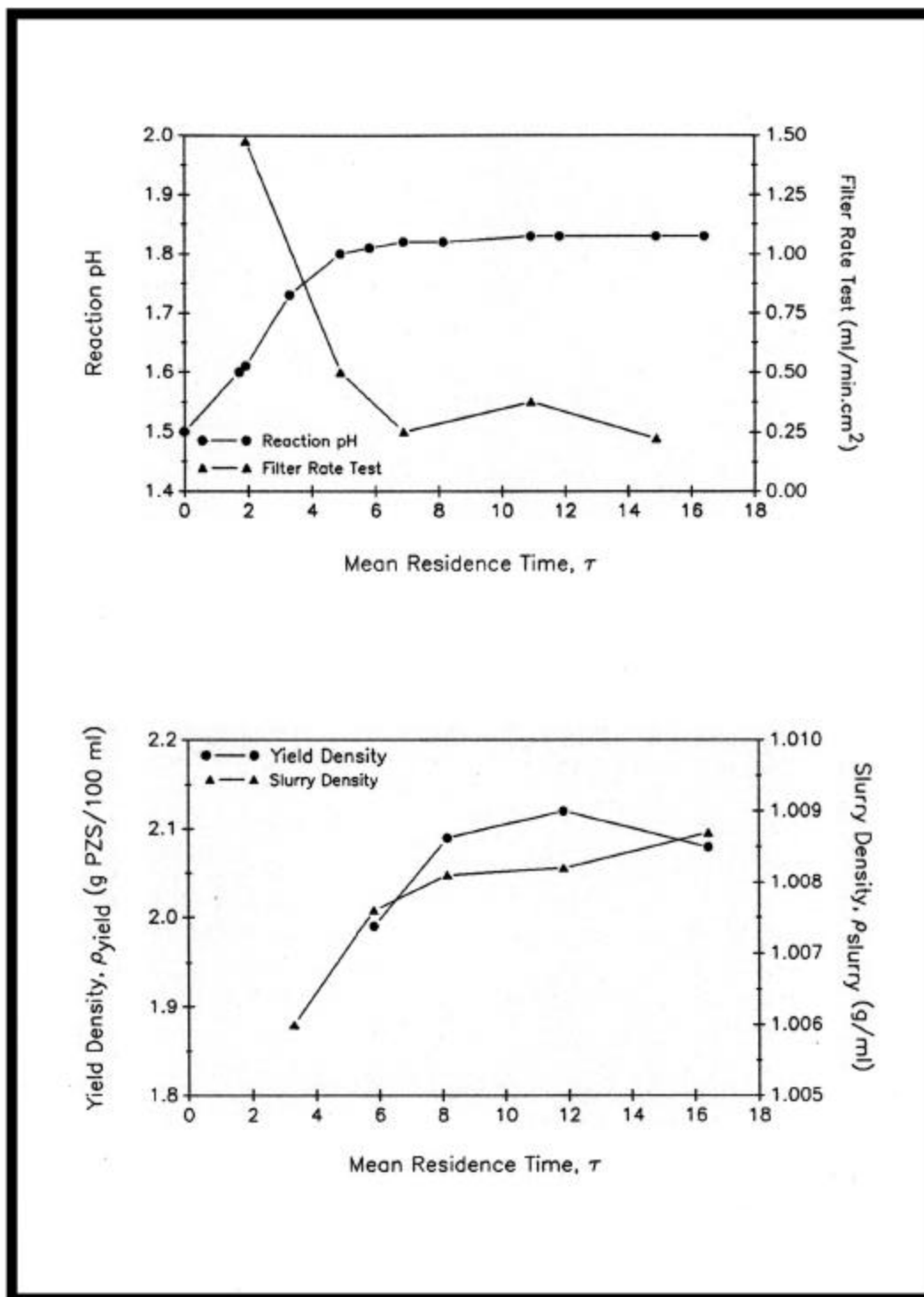


Figure 11: Steady state of four response variables for zirconium sulfate production Run #SS2. All density measurements were measured at $T=48^\circ\text{C}$. PZS = Pentazirconyl disulfate. ■

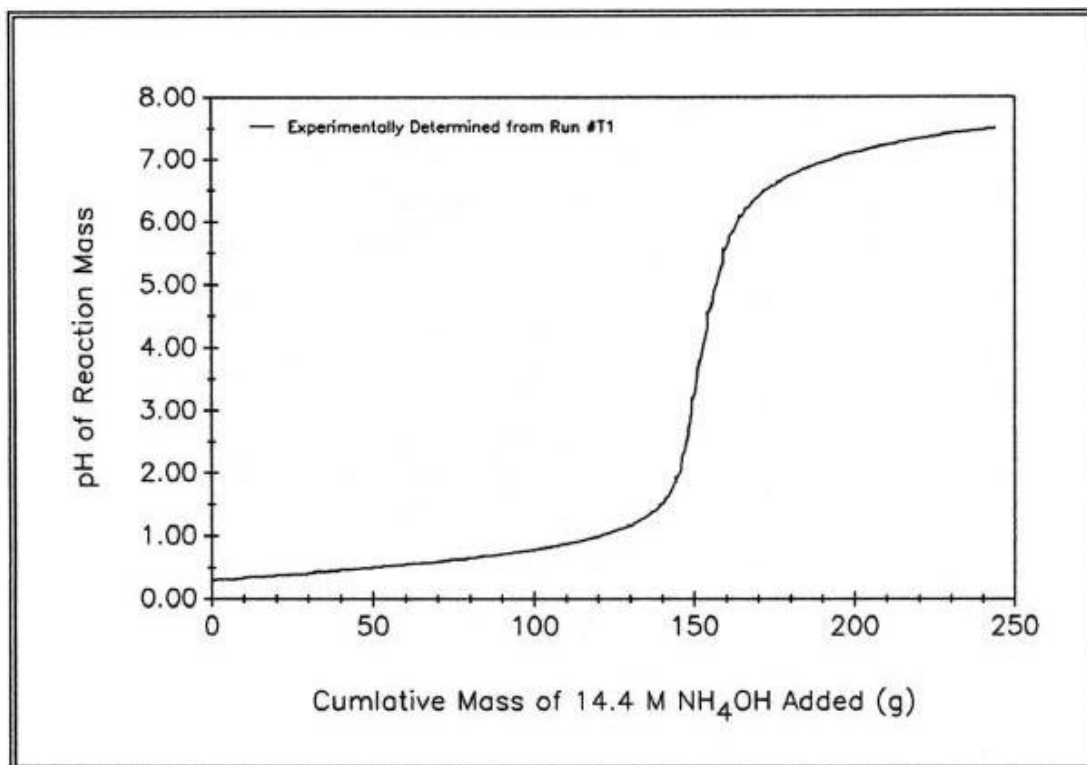


Figure 12: Acid/base titration curve for zirconium sulfate precipitation reaction at 95 °C. Reactor volume was initially charged with 2.01 kg of acid feed composed of 0.2 M $\text{ZrOCl}_2/(5/2)$ molar ratio of $\text{Zr}/\text{SO}_4/1$ N free acid (HCl).

The estimated percentage of steady state for these values are 98.9% for pH, 83% for FRT, 95.2% for η_{yield} and 99.9% for η_{slurry} . The relationship for steady state given in Equation (III-11) predicts that after t_6 you should be within 99.4 percent of steady state. Based upon these results, steady state is sufficiently established (i.e., 95% condition) for this system after 6 mean residence times when starting with a reactor which is charged with a 0.06 M HCl solution (pH=1.5).

III-5.0 REACTOR ACID/BASE BATCH TITRATION.

For the link between R' and pH to be made, a titration curve for the actual run conditions had to be generated. This entailed the initial charging of the reactor with 2.01 kg of a 0.2 M $\text{ZrOCl}_2/0.08$ M $\text{H}_2\text{SO}_4/1$ N free acid (HCl) solution. This acid solution was heated as rapidly as possible (taking ~15 min) to 95 °C while continually stirring at 1300 RPM's. The reactor configuration consisted of the draft tube insert and the stirrer shown in Figure 7. The internal layout for this configuration was shown in Figure 8. Once the acid mass was heated to temperature, many small concentrated base additions were made over short periods of time and the pH readings recorded on 2-second intervals. The base was added in 10 g aliquots at a rate of 5 g/ min, except in the range of the equivalence point where the aliquots were reduced to 5 g (at the same addition rate). The smaller aliquots of each

an increased sensitivity for the rapidly changing pH could be accounted for accurately. After each addition was made, an equilibration time of 3 min. was allowed for establishing the pH readings. The results of this titration, using the RC1™ for the conditions used to study the precipitation of zirconium sulfate within this thesis, is shown in Figure 12.

It now becomes possible to relate the reaction pH to R' by choosing a pH value of interest, relating that to the corresponding amount of NH₄OH necessary to achieve this value (the value on the x axis) and applying the following formula:

$$R' = \frac{2010 \text{ g Acid}}{X \text{ g NH}_4\text{OH}(0.273)} \quad (\text{III-12})$$

This curve serves as the basis for correlating the acid/base ratio to the reactor pH due to the inability to control pH using an internal pH probe (because of probe degradation).