

# Status Report on Estimation of Solubility for Zinc Silicates in PWR Primary Coolant



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# **Status Report on Estimation of Solubility for Zinc Silicates in PWR Primary Coolant**

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Technical Review, November 1999

EPRI Project Manager

P. Frattini

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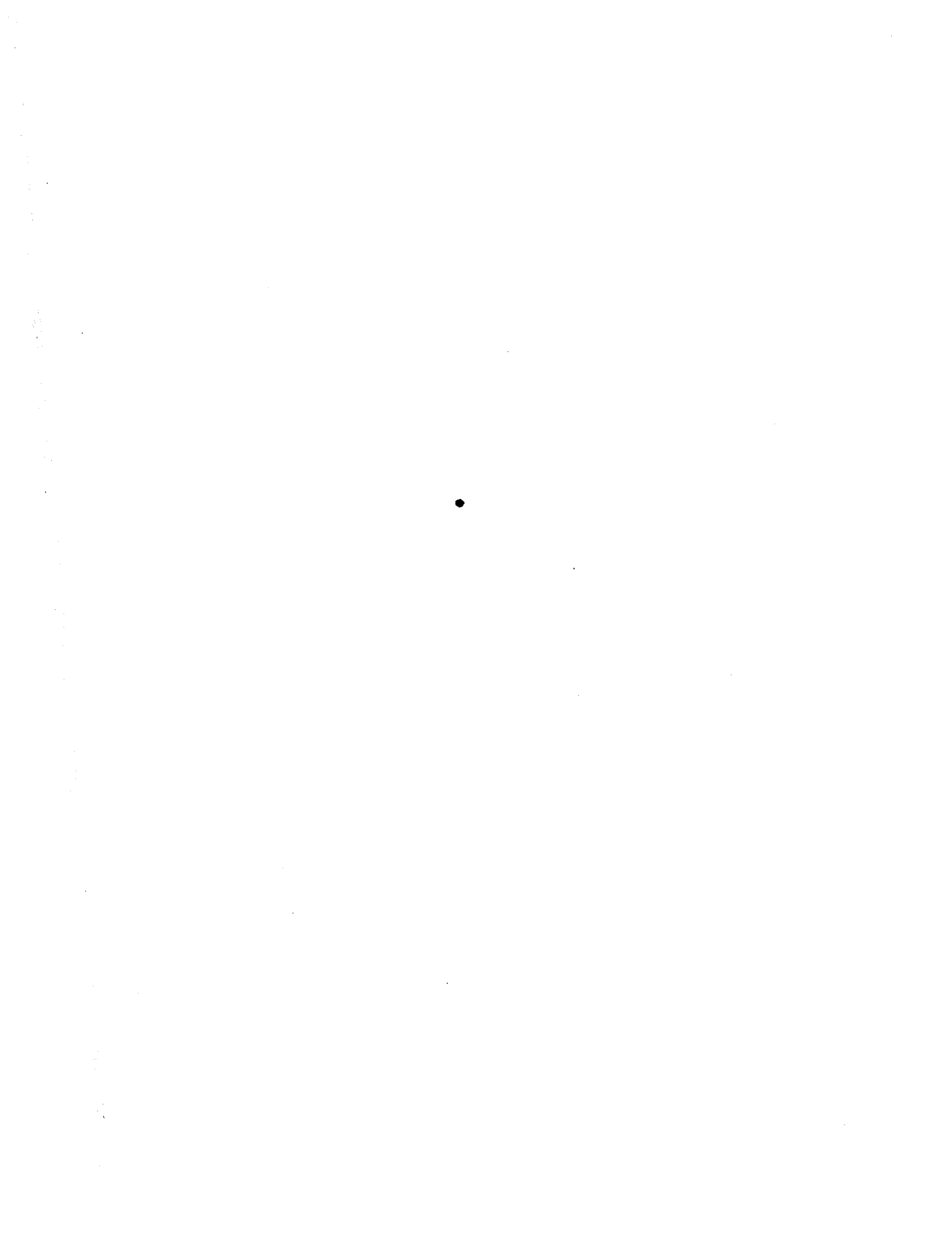
Lindsay and Associates  
47 E. Main Street  
Hopkinton, MA 01748

Principal Investigator  
W. T. Lindsay, Jr.

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# CONTENTS

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FOREWORD.....	ix
INTRODUCTION.....	1
BASIS FOR ESTIMATION.....	1
DATA AVAILABILITY.....	1
EQUATIONS FOR ESTIMATION OF SOLUBILITY OF ZINC OTHOSILICATE AND ZINC METASILICATE.....	3
CALCULATION OF ESTIMATED SOLUBILITIES.....	4
DISCUSSION.....	5
TASKS STILL TO BE COMPLETED.....	6
REFERENCES.....	7

# LIST OF FIGURES

---

FIGURE 1. PHASE DIAGRAM FOR SYSTEM $\text{SiO}_2\text{-ZnO-H}_2\text{O}$ FOR CONDITIONS AT THE BEGINNING OF A FUEL CYCLE .....	9
FIGURE 2. PHASE DIAGRAM FOR THE SYSTEM $\text{SiO}_2\text{-ZnO-H}_2\text{O}$ FOR CONDITIONS AT THE END OF A FUEL CYCLE .....	10
FIGURE 3. CHANGE OF ESTIMATED SILICA SOLUBILITY FROM ZINC ORTHOSILICATE DURING A FUEL CYCLE .....	11
FIGURE 4. EFFECT OF CHANGE OF AT-TEMPERATURE PH ON ESTIMATED SILICA SOLUBILITY FROM ZINC ORTHOSILICATE DURING A FUEL CYCLE .....	12

# LIST OF TABLES

---

TABLE 1. SAMPLE CALCULATION PRINTOUT.....	8
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## Foreword

Studies completed for *Revision 4* of the *PWR Primary Water Chemistry Guidelines* show that low concentrations of zinc in the PWR primary coolant may help to inhibit both PWSCC of Alloy 600 and out-of-core exposure rates. However, zinc may also cause detrimental effects if high concentrations of dissolved silica are present in the primary coolant, because zinc silicates may deposit on fuel surfaces creating harmful crud deposits. The current revision of the guidelines suggests that the concentration of silica in reactor water be kept less than 3000 ppb, subject to concurrence by fuel vendors. This technical review was prepared to provide estimates of zinc silicate solubility in support of the silica limit. The report concludes that zinc silicates will not be detrimental at or below the PWR Guidelines' silica limit. However, caution should be exercised in applying these results, because the values are theoretical estimates that are not based on experimental data.



STATUS REPORT ON  
ESTIMATION OF SOLUBILITY FOR  
ZINC SILICATES IN PWR PRIMARY COOLANT

W. T. Lindsay, Jr.  
Lindsay and Associates, Hopkinton, MA 01748  
April 2, 1999

## 1. INTRODUCTION

The addition of zinc to PWR primary coolant can be beneficial by slowing radiation field buildup and mitigating primary side stress corrosion cracking of Inconel steam generator tubing. However, plants with Boraflex fuel storage racks in the spent fuel pool can experience elevated levels of both reactive and colloidal silica in the pool water. Mixing of this water with reactor coolant during refueling operations can cause concentrations of dissolved silica in primary coolant to be relatively high during subsequent power operation. The benefits of zinc addition could be negated by detrimental effects if zinc silicate were to deposit on fuel surfaces, possibly consolidating crud deposits that would be otherwise benign.

The purpose of this work has been to estimate the solubility of zinc silicates in primary coolant. Such information may be helpful in assessment of possible consequences when zinc addition is implemented at plants that have difficulty in meeting target silica concentrations for primary coolant. Current guidelines suggest a plant-specific target of <3,000 ppb silica, subject to concurrence by fuel vendor [1].

## 2. BASIS FOR ESTIMATION

### 2.1. Data Availability.

Literature searches have not yet found a report of solubility measurement at relevant conditions for any zinc silicate. Several different zinc silicates are known to exist. Most prominent is willemite, which is zinc orthosilicate ( $Zn_2SiO_4$ ) with formal

composition  $2\text{ZnO}\cdot\text{SiO}_2$ . Also relatively well-known is a zinc metasilicate ( $\text{ZnSiO}_3$ ), for which the formal composition is  $\text{ZnO}\cdot\text{SiO}_2$ . There is mention in an index of X-ray diffraction patterns of a zinc pyrosilicate hydrate ( $\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7\cdot\text{H}_2\text{O}$ ), for which the formal composition would be  $4\text{ZnO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$ . This may be a form of hemimorphite, which is listed in the CRC Handbook [2] as having two crystalline forms with composition  $2\text{ZnO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ . It is possible that other zinc silicates and hydrates, with general composition  $a\text{ZnO}\cdot b\text{SiO}_2\cdot c\text{H}_2\text{O}$ , could exist at hydrothermal conditions. However, nothing has been found about this possibility.

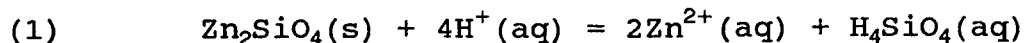
Thermodynamic data given in the NBS Tables [3] for zinc orthosilicate include enthalpy of formation, free energy of formation, entropy and heat capacity, all at 298.15 K. These data are adequate, in combination with existing data for dissolved zinc and silicate species, for estimation of the solubility of  $\text{Zn}_2\text{SiO}_4$  as a function of temperature. Only one thermodynamic datum is given for zinc metasilicate: enthalpy of formation at 298.15 K. No thermodynamic data useful for the present purpose have been found for any other zinc silicate compositions.

Several possibilities for extrapolation of zinc oxide solubility to primary coolant conditions are given in a recent report to EPRI [4]. Of these, the Case C extrapolation is appropriate for initial evaluation of the zinc silicate situation. This extrapolation is based on all relevant data for zinc oxide solubility. Thermodynamic data are available from Case C for equilibria between solid zinc oxide and all dissolved zinc species.

The solubility of  $\text{SiO}_2$  (quartz) can be calculated from the recently revised entry for 688) SiO2 in MULTEQ database Version 3.0 [5]. Thermodynamic data for dissolved silicic acid ( $\text{H}_4\text{SiO}_4$ ) and several other silicate species in solution are available in this and earlier versions of the MULTEQ database.

## 2.2. Equations for Estimation of Solubility of Zinc Orthosilicate and Zinc Metasilicate.

The solubility of zinc orthosilicate is represented by

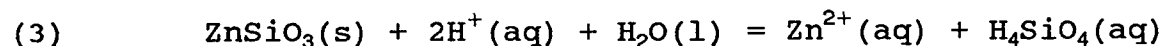


This is an isocoulombic reaction. The solubility product as a function of temperature can be derived from the change of standard enthalpy and standard entropy at 298.15 K, as calculated from data in the NBS Tables [3]. The result is

$$(2) \quad \log K_{\text{sp}}(1) = 7294.04/T - 9.1724$$

Equilibria between  $\text{Zn}^{2+}(\text{aq})$  and other dissolved zinc species are given by the Case C set of equations in Table 7 of Ref. [4].

The dissolution reaction for zinc metasilicate is



This also is an isocoulombic reaction. However, the NBS Tables provide information only for calculation of standard enthalpy change at 298.15. A value for standard entropy change (or change of standard free energy) is needed additionally for determining a temperature dependence for the solubility product.

An estimate can be made for the entropy of  $\text{ZnSiO}_3(\text{s})$  at 298.15 K by a method outlined by Latimer [6]. The Latimer estimation method was evaluated for several other metasilicates by comparison with data that are available in the NBS Tables. Results are given below.

$S^\circ(298.15)$ , J/mol-K:	<u>Estimate</u>	<u>NBS Tables</u>
MgSiO <sub>3</sub> (s)	75.74	67.74
CaSiO <sub>3</sub> (s)	82.85	81.92
SrSiO <sub>3</sub> (s)	94.15	96.7
BaSiO <sub>3</sub> (s)	101.26	109.6
CdSiO <sub>3</sub> (s)	97.9	97.5

Except for  $\text{MgSiO}_3$ , the agreement is reasonable. The Latimer-method estimate for  $\text{ZnSiO}_3(\text{s})$  is  $89.55 \text{ J/mol-K}$ . Accepting this, the following equation is derived for temperature dependence of the solubility product for Reaction (3):

$$(4) \quad \log K_{\text{sp}}(3) = 3993.86/T - 4.7826$$

### 3. CALCULATION OF ESTIMATED SOLUBILITIES

A BASIC computer program was written for calculation of pH, species concentrations and other data for high-temperature aqueous solutions in equilibrium with solid phases  $\text{SiO}_2$ ,  $\text{ZnO}$ ,  $\text{Zn}_2\text{SiO}_4$  and  $\text{ZnSiO}_3$ , either singly or in pairs of two solids. Equations (2) and (4) were used, along with equations for solubility, hydrolysis and polymerization equilibria for the various solution species.

The calculations were carried out for solutions containing boric acid and lithium hydroxide at several sets of conditions corresponding to Modified Chemistry variations during a fuel cycle. Equilibrium constants for ionization and polymerization reactions among dissolved borate species were NOT those of MULTEQ database Versions 3.0 or 2.77. Instead, these constants were based on the ORNL speciation model for borates, which has been employed traditionally in calculations related to primary coolant. However, the constants used here for formation of the three borate polyions differ slightly from the corresponding constants listed on Page A-3 of Ref. [1]. The differences are due to a correction recognized in the early 1990's by R. E. Mesmer of ORNL and subsequently recommended by C. F. Baes, Jr. [7].

Another difference from Appendix A of Ref. [1] relates to activity coefficients. The calculations here made use of the MULTEQ model for activity coefficients of ionic and neutral species, except that special status for the activity coefficients of  $\text{H}_3\text{BO}_3(\text{aq})$  and  $\text{H}_4\text{SiO}_4(\text{aq})$  was disabled.

Table 1 is a sample printout from the BASIC program that generated the solubility estimates for  $Zn_2SiO_4$ ,  $ZnSiO_3$ ,  $SiO_2$  and  $ZnO$ . Approximately 200 such calculations were made.

Figure 1 shows the results in the form of a phase diagram for temperatures 275-350°C at conditions corresponding to the beginning of a fuel cycle. Figure 2 shows the same information for the end of a fuel cycle. These two figures are very similar. There are slight differences, but they are of little significance.

Figure 3 shows the estimated magnitude of ppm  $SiO_2$  that would be needed to precipitate  $Zn_2SiO_4$  from solutions containing either 40 or 80 ppb total Zn, at 300° and 350°C, during progression of a fuel cycle. Figure 4 shows the same information plotted against pH at temperature for the four sets of ppm B and ppm Li that are indicated on Fig. 3.

Estimated solubilities of silica from  $ZnSiO_3$ , when it was selected as the solid phase, were approximately 100 times higher than for  $Zn_2SiO_4$  at the same dissolved zinc concentration and other conditions. These results indicate that  $ZnSiO_3$  is not a stable phase at PWR conditions. It could be more stable than  $Zn_2SiO_4$  in very acid solutions.

Representative calculations with  $ZnO$ ,  $Zn_2SiO_4$  and  $SiO_2$  solid phases were checked by MULTEQ v. 2.25 with a specialized database modified to correspond to thermodynamic data used with the BASIC program.

#### 4. DISCUSSION

Figures 1 and 2 predict that precipitation of  $Zn_2SiO_4$  should not occur with dissolved silica at 3000 ppb  $SiO_2$  at any temperature or pH experienced within primary coolant or at fuel surfaces during a fuel cycle, even with zinc concentration as high as 80 ppb. If zinc concentration is limited to 40 ppb, much higher dissolved

silica concentrations would be needed for precipitation.

Calculated solubilities increase with temperature, indicating an effective positive temperature coefficient. However, this result is due largely to increase of coolant pH as temperature increases.

The lowest calculated silica solubility was about 4700 ppb  $\text{SiO}_2$ , which was at  $275^\circ\text{C}$  at the beginning of a fuel cycle for a solution saturated with both  $\text{Zn}_2\text{SiO}_4$  and  $\text{ZnO}$ . The zinc concentration calculated for this set of conditions (with the Case C solubility extrapolation for  $\text{ZnO}$ ) was about 88 ppb Zn.

Although these results do not predict that a problem will occur if zinc addition is implemented when dissolved silica is at or near target concentrations suggested by the current guidelines, it must be remembered that the solubilities calculated here are unconfirmed estimates. They are not based on experimental information at any relevant temperature. They may also be incomplete, in that unknown other solid phases of the general composition  $a\text{Zn}\cdot b\text{SiO}_2\cdot c\text{H}_2\text{O}$  could be less soluble than  $\text{Zn}_2\text{SiO}_4$  at hydrothermal conditions.

#### 5. TASKS STILL TO BE COMPLETED

1. Expand literature searches for experimental solubility information and for more thermodynamic data that may be useful in solubility estimation.
2. Devise methods for estimating stability and solubility of zinc silicates that may be postulated, by analogy with other divalent metal silicate compounds, to exist in the range of general compositions.
3. Perform calculations of estimated solubilities for zinc silicates for which additional information may be found, or for postulated other zinc silicates.
4. Prepare final report.

## 6. REFERENCES

1. PWR Primary Water Chemistry Guidelines - Revision 4 - Volume 1: Power Operation. EPRI Report TR-105714, V1, Rev. 4, P. J. Millett et al., editors, January, 1999. Table 3-4, p. 3-17.
2. D. R. Lide, editor-in-chief, "CRC Handbook of Chemistry and Physics", 72nd. Edition, 1991-1992, p. 4-113.
3. D. D. Wagman et al. "The NBS Tables of Chemical Thermodynamic Properties," J. Physical and Chemical Reference Data, Volume 11, 1982, Supplement No.2.
4. W. T. Lindsay, Jr., "Update on Solubility of Zinc Oxide at PWR Primary Coolant Conditions," Report to EPRI Nuclear Power Division from Lindsay and Associates, Hopkinton, Ma 01748, dated October 8, 1998.
5. MULTEQ: Equilibrium of an Electrolytic Solution with Vapor-Liquid Partitioning and Precipitation: The Database. EPRI Report NP-5561-CCML, Volume 2, Rev. 4, 4521. (Draft of Final Report, dated March, 1999, prepared by J. H. Alexander and D. U. DeCastro.)
6. W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," 2nd Edition (New York, Prentice Hall, 1952). Appendix III, Methods for Estimation of Entropy Values, pp. 359-369.
7. C. F. Baes, Jr., "Boric Acid Equilibria. The Mesmer Correction", memo to P. J. Millett, May, 1992.

TABLE 1  
SAMPLE CALCULATION PRINTOUT

SOLUBILITY CALCULATION FOR ZINC SILICATES. Solid phase(s) are:

Zn<sub>2</sub>SiO<sub>4</sub>  
 Temp. (C) = 300      pH = 6.907837  
 Total Li = 3.170486E-04      Total B = .1109981  
 Total Zn (CALC) = 6.118981E-07      Total Si (CALC) = 5.531654E-04

Species distribution (molal concentrations):

B(OH)3(aq)	= .1106806	% of total B = 99.714
B(OH)4-	= 2.415819E-04	% of total B = .2176452
B2(OH)7-	= 3.363399E-05	% of total B = 6.060284E-02
B3(OH)10-	= 3.202125E-06	% of total B = 8.654541E-03
B4(OH)14--	= 1.629134E-09	% of total B = 5.870856E-06
Li+	= 3.163343E-04	% of total Li = 99.77472
LiOH	= 7.142113E-07	% of total Li = .2252687
Zn++	= 4.310446E-11	% of total Zn = 7.044385E-03
Zn(OH)+	= 3.478794E-08	% of total Zn = 5.685251
Zn(OH)2(aq)	= 5.338173E-07	% of total Zn = 87.23958
Zn(OH)3-	= 4.324976E-08	% of total Zn = 7.068131
Zn(OH)4--	= 0	% of total Zn = 0
H4SiO4(aq)	= 5.502558E-04	% of total Si = 99.47402
H3SiO4-	= 2.909483E-06	% of total Si = .5259698
H2SiO4--	= 4.306646E-12	% of total Si = 7.78546E-07
H6(SiO3)4--	= 1.158989E-16	% of total Si = 8.380781E-11
H+	= 1.236411E-07	
OH-	= 3.515384E-05	

Ionic strength = 3.16512E-04  
 Water activity = .997987  
 Gamma = .9510485  
 Gamma zero = 1.000162

Log K<sub>SO</sub>(Zn) = 3.751391  
 Log K<sub>O1</sub>(Zn) = -3.956459  
 Log K<sub>O2</sub>(Zn) = -9.677455  
 Log K<sub>O3</sub>(Zn) = -17.71942  
 Log K<sub>O4</sub>(Zn) = -28.82378

Log K<sub>sp</sub>(SiO<sub>2</sub>) = -1.957198  
 Log K<sub>sp</sub>(ZnSiO<sub>3</sub>) = 2.185663  
 Log K<sub>sp</sub>(Zn<sub>2</sub>SiO<sub>4</sub>) = 3.553839  
 Log K<sub>O1q</sub>(Si) = 2.176331  
 Log K<sub>O2q</sub>(Si) = .7562094  
 Log K<sub>O42q</sub>(Si) = 5.960736

ppm B = 1200      ppm Li = 2.2  
 ppb Zn = 39.99978  
 ppm SiO<sub>2</sub> = 33.24524

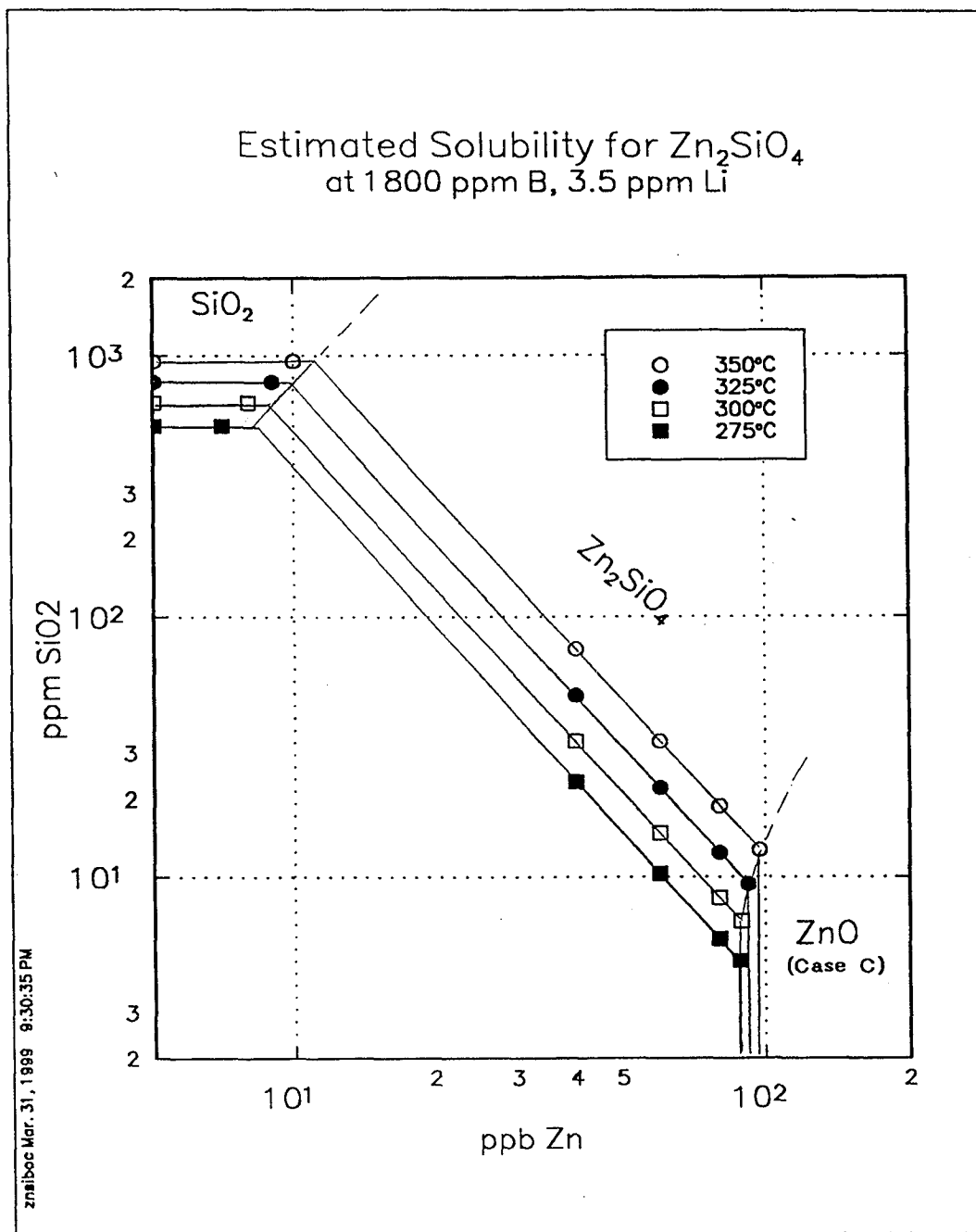


Figure 1. Phase diagram for system  $SiO_2$ - $ZnO$ - $H_2O$  for conditions at the beginning of a fuel cycle.

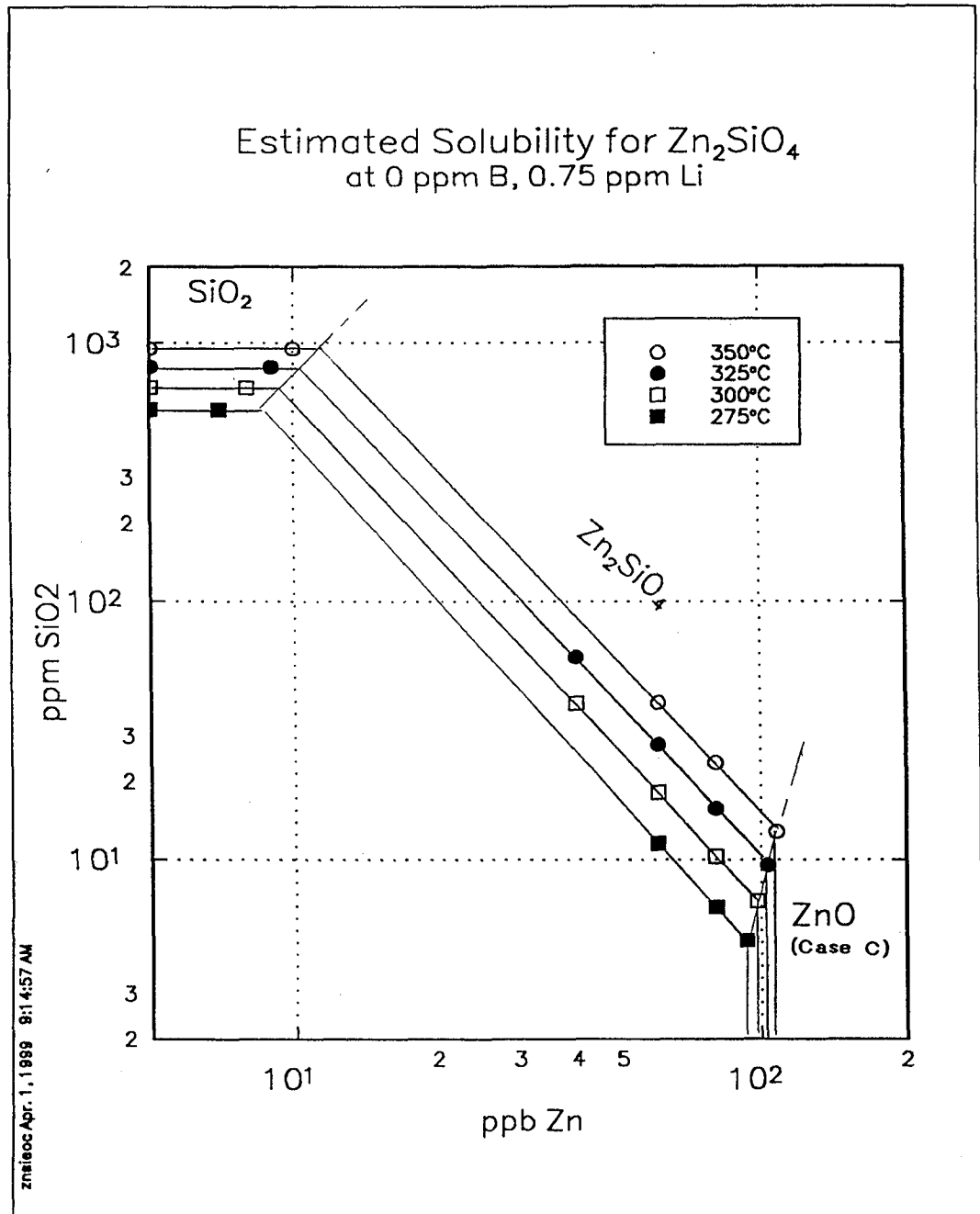


Figure 2. Phase diagram for the system  $SiO_2$ - $ZnO$ - $H_2O$  for conditions at the end of a fuel cycle.

### Estimated Silica Solubility from $Zn_2SiO_4$ Variation during fuel cycle

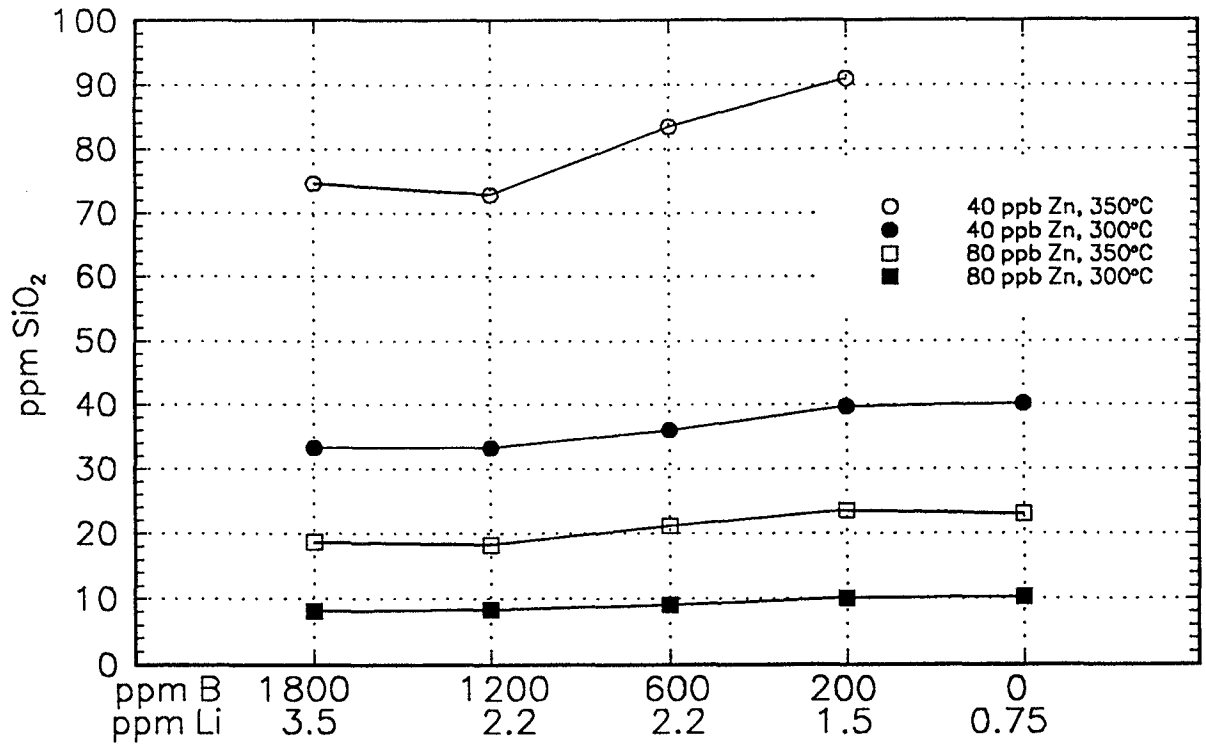


Figure 3. Change of estimated silica solubility from zinc orthosilicate during a fuel cycle.

### Estimated Silica Solubility from $Zn_2SiO_4$ Variation with pH change during fuel cycle

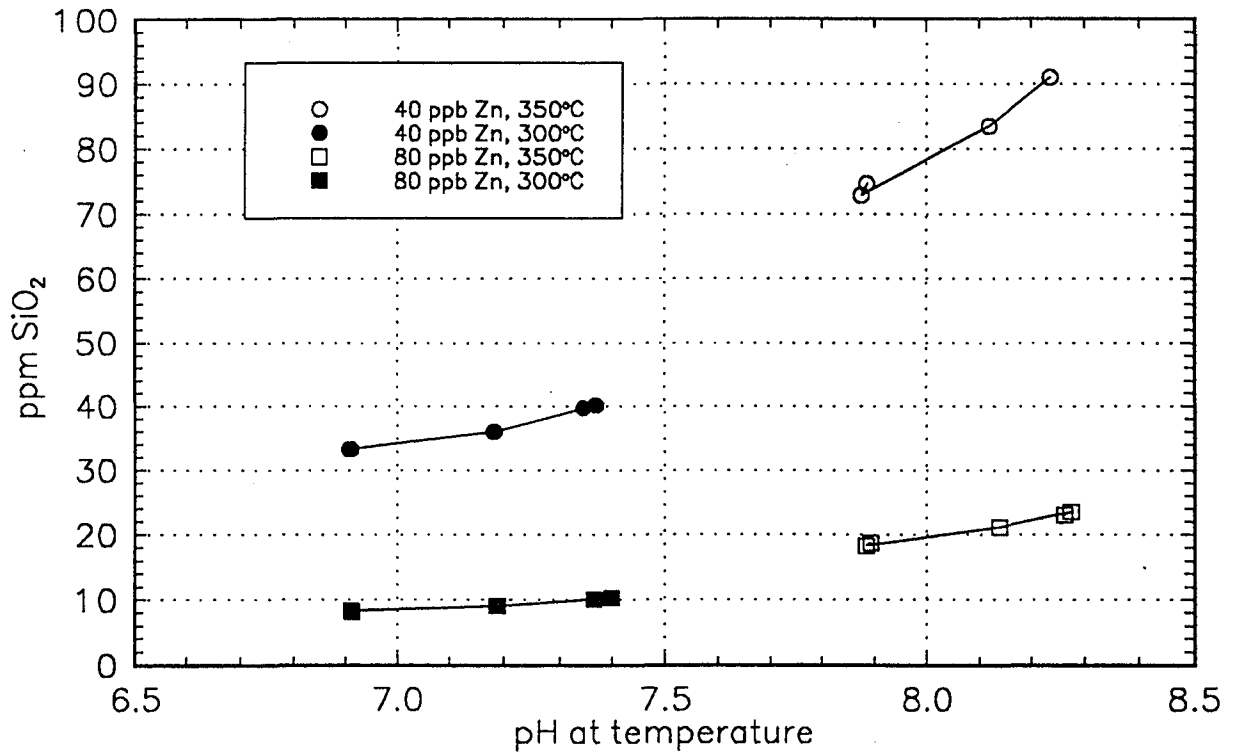
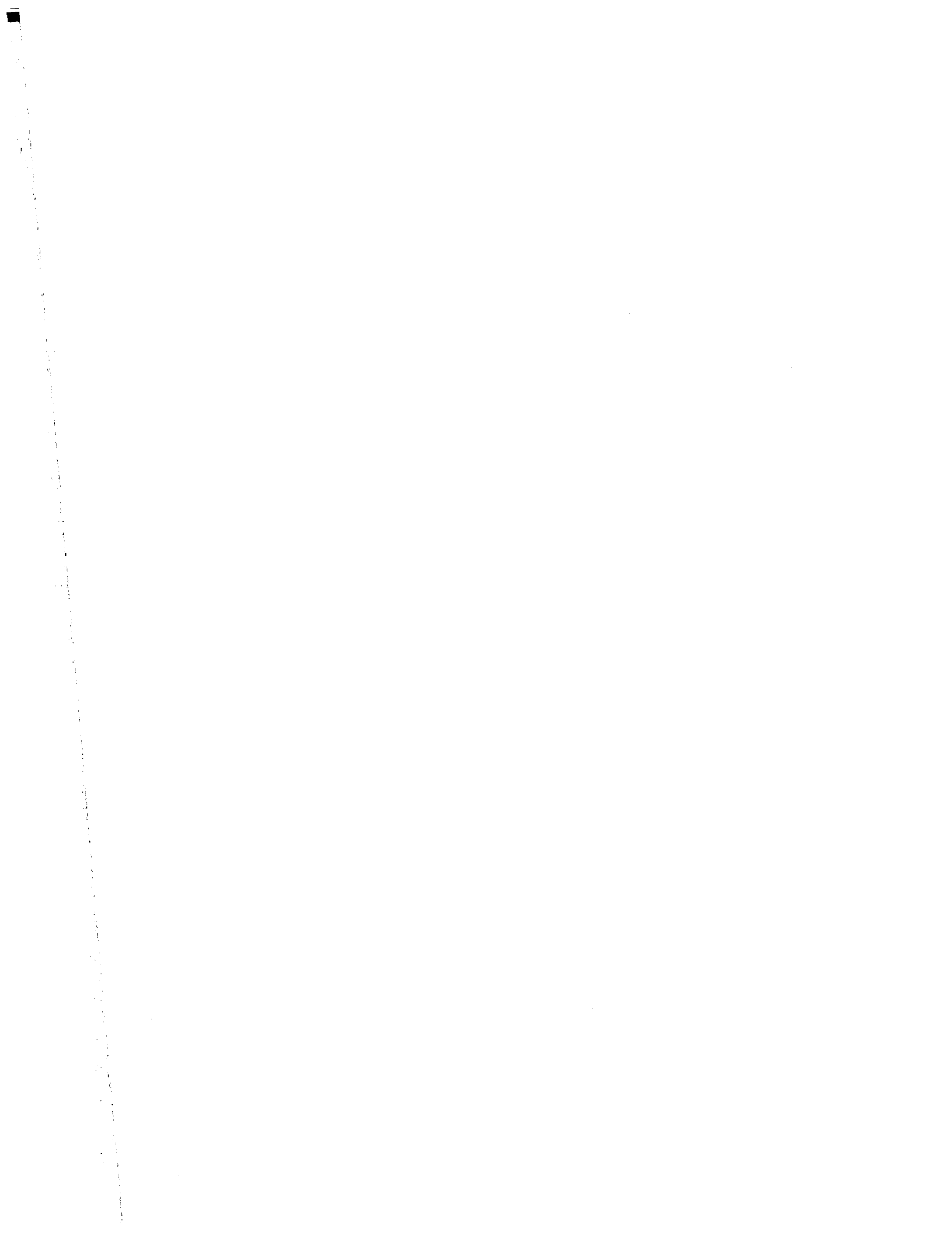


Figure 4. Effect of change of at-temperature pH on estimated silica solubility from zinc orthosilicate during a fuel cycle.





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