Solubility of Boron Compounds in Nitric Acid Solutions

by

J. H. Gray

Westinghouse Savannah River Company

Savannah River Site

Aiken, South Carolina 29808

DOE Contract No. **DE-AC09-96SR18500**

This paper was prepared in connection with work done under the above contract number with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P. O. Box 62, Oak Ridge, TN 37831; prices available from (423) 576-8401.

Available to the public from the National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

WSRC-TR-98-00426

Revision 0

Solubility of Boron Compounds in Nitric Acid Solutions (U)

By

John H. Gray

Issued: 11/19/98

Technical Reviewer

Alice M. Murray
A. M. Murray

November 19, 1998
Date

UNCLASSIFIED

DOES NOT CONTAIN
UNCLASSIFIED CONTROLLED
NUCLEAR INFORMATION

ADC &
Reviewing
Official: Alan Paul Clarke Sr. Eng A
(Name and Title)
Date: 11/19/98

Westinghouse Savannah River Company
Building 773-A
Aiken, SC 29808

Prepared for the U. S. Department of Energy under Contract DE-AC09-96SR18500

Table of Contents

Section	Page
SUMMARY.....	1
INTRODUCTION.....	1
DISCUSSION.....	2
CONCLUSIONS.....	2
REFERENCE.....	2
TABLE Table 1, Precipitation of Boron Solids.....	3

Solubility of Boron Compounds in Nitric Acid Solutions (U)

John H. Gray

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

SUMMARY

A series of laboratory experiments has been performed to determine flowsheet conditions for formation of boron solids during processing of glovebox floor sweepings (FS) and sand, slag, and crucible (S,S,&C) materials in canyon dissolvers. The precipitation of a boron compound (KBF₄) was identified during the flowsheet development work for processing Rocky Flats S,S,&C materials at Savannah River. The subsequent series of laboratory experiments has focused on flowsheet conditions planned for the dissolution of glovebox floor sweepings in S,S,&C solutions.

The concentrations of potassium fluoride (KF) and total fluoride were established where precipitation of boron solids would and would not occur during the processing of floor sweepings. Other variables such as changes in nitric acid and iron concentrations were found to have no impact on formation of boron solids. Results presented in Table 1 indicate that boron solids will not form at 0.22 molar KF and 0.30 molar total fluoride during processing of floor sweepings and at 0.22 molar KF and 0.32 molar total fluoride during processing of S,S,&C materials.

INTRODUCTION

The initial dissolver solution conditions for processing floor sweepings in the canyon are different (Ref 1) than those being used for the dissolving of S,S,&C materials. This difference is because the calcium fluoride (CaF₂) present in S,S,&C materials is sufficient to raise total fluoride concentrations to required levels. However, no CaF₂ is present in floor sweepings and the required starting total fluoride concentrations will be achieved by the additions of KF to the floor sweepings flowsheet. This KF addition combined with the (apparent) limited KBF₄ solubility has made it necessary to identify flowsheet conditions which would result in no KBF₄ precipitation during processing of floor sweepings.

DISCUSSION

Table 1 presents results from both actual S,S,&C dissolution studies and cold experiments which simulated proposed dissolver solution concentrations for processing floor sweepings in canyon dissolvers. It was during laboratory experiments SSC-Pu-1 and SSC-Pu-2 that KBF₄ solids were observed. At 0.22 molar KF and 0.32 molar total fluoride concentration, no KBF₄ solids formed. Only when the total fluoride concentration reached 0.40 molar did the white KBF₄ crystals form.

The starting solution concentrations of 9.2 molar nitric acid, 0.03 to 0.12 molar iron, and 2.2 grams boron per liter are common to both the floor sweepings and S,S,&C flowsheets. The 0.17 molar KF is the expected KF concentration during processing of floor sweepings. The 0.22 molar KF is the expected maximum KF concentration. Incremental additions of CaF₂ to the starting 0.22 molar KF solutions resulted in no KBF₄ precipitation at 0.30 molar total fluoride and the formation of the trace amounts of KBF₄ solids at a total fluoride concentration of 0.33 molar. Results from experiment SSC-Pu-1 agree well with the observations made during experiments FS-COLD-3 and FS-COLD-4.

CONCLUSIONS

- (1) Flowsheet conditions have been identified for formation of no KBF₄ solids during the processing of floor sweepings and S,S,&C materials.
- (2) Addition of a floor sweepings batch to a dissolver solution which has already processed multiple S,S,&C batches is possible without the formation of KBF₄ solids. This addition is possible because the initial (and total) KF concentration in S,S,&C solutions has been 0.075 molar and increases in total fluoride concentrations are from CaF₂ additions and not KF. Results from a successful dissolution of floor sweepings into a solution containing two dissolved S,S,&C batches will be reported later.
- (3) Addition of a S,S,&C batch to a dissolver solution containing a dissolved floor sweepings batch may be difficult to control. This difficulty is because the starting total KF concentration in floor sweepings solutions is high, 0.15-0.22 molar, and because the exact amount of total fluoride in S,S,&C batches may not be known well enough to remain below the upper limit of 0.30-0.33 molar total fluoride.

REFERENCE

- (1) "The Dissolution of Glovebox Floor Sweepings in F-Canyon Dissolvers" (U), John H. Gray, 10/9/98

TABLE 1 PRECIPITATION OF BORON SOLIDS

EXPT #	HNO3 (M)	KF (M)	Fe (M)	Total F (M)	Boron Solids
FS-Cold-1	9.2	0.17	0.12	0.32	None
FS-Cold-2	9.2	0.17	0.12	0.36	Trace
FS-Cold-3	9.2, 14.1	0.22	None	0.30	None
FS-Cold-4	9.2, 14.1	0.22	None	0.33	Trace
FS-Cold-5	9.2, 14.1	0.22	None	0.36	Many
FS-Cold-6	9.2, 14.1	0.22	0.03	0.33	Trace
SSC-Pu-1	8.8	0.22	0.12	0.32	None
SSC-Pu-2	8.6	0.26	0.12	0.40	Many

WSRC INTERNAL DISTRIBUTION

Distribution

N. Barnett, 707-F
J. E. Batton, 707-7F
D. E. Buxton, 707-F
T. G. Campbell, 221-F
W. H. Clifton, 221-14F
O. M. Ebra-Lima, 707-F
F. R. Graham, 773-A
J. Gregg, 707-F
W. R. Hinz, 730-A
A. M. Jwayyed, 703-F
D. G. Karraker, 773-A
E. A. Kyser, 773-A
R. R. Livingston, 773-A
A. M. Murray, 773-A
J. A. Parker, 221-14F
J. M. Poglitsch, 221-14F
M. R. Price, 221-F
T. S. Rudisill, 773-A
J. B. Schaade, 703-F
D. Stimac, 703-F
M. C. Thompson, 773-A
G. J. Winkler, 703-F
C. R. Wolfe, 773-A
S. A. Yano, 704-2H
SRTC Records, 773-52A