Solubility of Boron Compounds in Nitric Acid Solutions

by

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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 is 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

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