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CONTINUOUS DISSOLUTION OF PLUTONIUM-BEARING SLAG AND CRUCIBLE RESIDUES

H. W. CROCKER

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CONTINUOUS DISSOLUTION OF PLUTONIUM-BEARING SLAG AND CRUCIBLE RESIDUES

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CONTINUOUS DISSOLUTION OF PLUTONIUM-BEARING SLAG AND CRUCIBLE RESIDUES

INTRODUCTION

~~The new Plutonium Reclamation Facility (PRF), Project CAC-880,~~ a proposed plutonium recovery facility will process slag and crucible reduction residues on a continuous basis.[1] In support of this work, a full-scale continuous dissolver has been successfully operated with a simulated plant feed consisting of new crucibles and solid technical-grade reagents.[2] The simulated feed tests were conducted in a "cold" pilot plant, therefore plutonium could not be used. Actual demonstration of plutonium-bearing slag and crucible residue dissolution was desired to confirm the proposed continuous flow sheet.

The purpose of this report is to present the experimental work on continuous dissolution of plutonium-bearing slag and crucible residues generated from actual plant operation.

A prototype continuous dissolver is to be installed in the present Recuplex Facility to demonstrate the operability and capacity factors for plutonium-bearing slag and crucible dissolution.

SUMMARY AND CONCLUSIONS

Laboratory runs have demonstrated successful dissolution of plutonium-bearing slag and crucible residues. The plutonium recovery was quantitative.

Vigorous reaction during initial dissolution of each solids charge caused formation of large quantitites of reaction foam. While the foam subsides in a few moments, the foam volume easily could result in a boilover from the dissolver. Charging of smaller batches more frequently ~~could~~ will minimize ~~eliminate~~ the problem.

All the experimental runs exhibited the formation of a residual solids heel in the dissolver. Since heel dissolution is slow, periodic dissolver clean-out runs will be required to maintain a low heel volume. Any excessive

solids heel buildup can be removed and dissolved in a lenghty batch treatment using 4M HNO_3 or 6M HCl. The residue in a 32-hour continuous run was eight per cent by weight of the solids charged.

It was determined that a 27.5 g/l ~~IO_3~~ iodate concentration was required in the dissolver overflow solution to precipitate plutonium iodate. The iodate concentration in the continuous dissolver is much less ~~that~~ than this value (< 5 g/l); therefore, formation of this inextractable precipitate should not be encountered.

Dissolver overflow solution adjusted to solvent extraction feed ~~specifications~~ composition was contacted with 20 per cent TBP - 80 per cent CCl_4 (volume basis). Four stages of extraction reduced the plutonium concentration in the aqueous feed to 0.003 g/l. Storage of feed material for five days did not effect the plutonium extraction. The presence of up to 0.08M titanium or 0.3M sulfate did not decrease the extractability of the plutonium.

~~RECOMMENDATIONS~~

~~The following modifications to the PRF process flow diagram (1) (SK-2-18400) are recommended:~~

1. ~~Substitute 72 per cent ANN for the indicated 62 per cent ANN in the chemical addition stream No. 8.~~
2. ~~Add the excess water (now available by using the 72 per cent ANN in stream No. 8) to the dissolver feed stream No. 2. This eliminates the gelatinous suspension in the dissolver overflow stream.~~
3. ~~Substitution of 1M HF as the stripping agent in the CO column in lieu of the $Fe(NH_4)_2SO_4)_2$ - $NH_2OH \cdot 1/2H_2SO_4$ - NH_2SO_3H strip, and subsequent blending of the plutonium bearing solution into the CAF stream. The HF should, of course, be complexed with ANN prior to blending. The change to an HF strip has previously been approved for use in Project CAC 880.~~

DISCUSSION

Equipment

A schematic diagram of the slag and crucible dissolution equipment is shown in Figure 1. A two-liter boiling flask equipped with CO_2 sparge, solution removal dip tube, overhead reflux condenser, acid feed inlet, and solids charging port was used in all the experiments. Dissolver overflow solution was removed via the dip tube and sampled in the overflow solution receiver. Sampled overflow solution was then transferred to a six-liter storage vessel. Acid feed was supplied from a heated vessel. Any liquid that carried past the reflux column was collected in a distillate receiver. Normal solution volume in the dissolver is one liter, contrasted to the 27.5 liter volume in the proposed plant units. ~~Therefore, a scale-down factor of 8.64×10^{-2} (1/27.5)~~ a processing basis of ~~250 grams of solid~~ was used in the experimental runs. The proposed solid feed to the continuous dissolver has the following chemical composition:

Chemical	Weight Per Cent
MgO	42.8
CaF_2	30.9
CaI_2	1.3
Ca	3.8
Fe	8.9
$Pu+PuO_2$	<12.3

Normal operation of the plant units will be to charge a can of slag and crucible to the dissolver. The ~~can submerges into the solution~~ charge reacts vigorously, causing part of the solution to overflow out of the dissolver. When the ~~crucible can dissolves~~ reaction subsides, the solution level in the dissolver drops below the overflow point. Continual addition of feed acid to the dissolver builds up the solution level. Solution level reaches the overflow point just prior to charging of the next can of solids. To simulate the plant-type operation, the following procedure was used in the continuous runs:

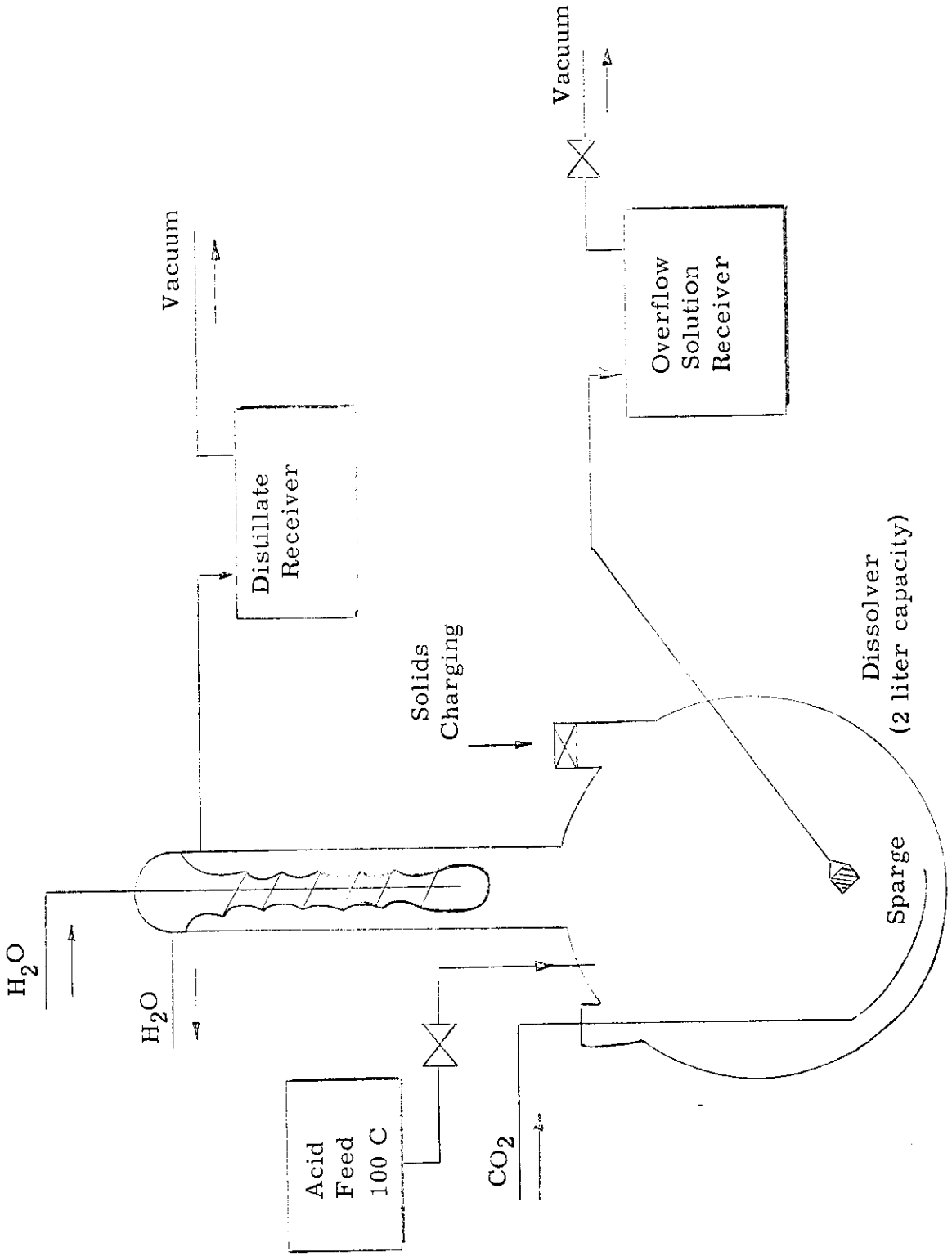

FIGURE 1

a. Charge solids.
b. Add feed acid.
c. Dissolve curcible material for specified time.
d. Remove specified volume of solution via the dip tube.
e. Repeat steps (a) through (d).

Experimental Dissolution Runs

Two 60- to 180-gram batch scouting runs were made to confirm that the crucible residue and plutonium would dissolve readily at the continuous flow sheet conditions[1, 3] which utilize a lower acid concentration than conventional batch dissolution. Plutonium and residue dissolution was quantitative in one hour. Dissolver overflow solution was used for the dissolution.

Three continuous dissolution runs of 8, 27, and 32 hours duration were completed. The dissolution run data are presented in Table I. The first two runs were at the tentative flow sheet conditions for the proposed recovery facility[1] specified in SK-2-18400. In each case the plutonium was quantitatively dissolved. The dissolver overflow product from the first two continuous runs was a viscous solution which contained approximately 25 volume per cent of suspended gelatinous solids. The material appeared to be a silica-gel and contained large amounts of ~~aluminum~~ Al, ~~magnesium~~ Mg, ~~calcium~~ Ca, ~~silica~~ Si, and ~~iron~~ Fe. On the final continuous run, additional dilution water was added to the acid feed to minimize the amount of gelatinous material in the dissolver overflow. The addition of dilution water successfully eliminated the formation of gelatinous suspensions without affecting the plutonium and residue dissolution. The dilution water can be incorporated into the dissolution step flow sheet without affecting the resulting solvent extraction feed composition. ~~This is done by using 75 per cent ANN in lieu of 62 per cent ANN in the chemical adjustment step (stream 8, SK-2-18400). The resulting available water can then be added to the dissolver feed solution (stream 2, SK-2-18400).~~

TABLE I

CONTINUOUS DISSOLUTION OF SLAG AND CURCIBLE RESIDUE

Run No.	Run Duration (Hours)	Total Solids Charged (Grams)	Average Dissolver Overflow Composition			Solids Residue Heel (Grams)	Pu Charged (Grams)	Pu Recovered (Grams)
			HNO_3 (M)	I_2 as I^- (g/l)	I_2 as IO_3 (g/l)			
CD-3	8	1197	3.5	0.6	2.5	130	12	13
CD-4	27	4851	4.0	0.7	2.0	300	20	31
CD-5	32	6135	3.6	2.0	0.5	500	104	100

Note: 1. Solids feed addition was 63 grams of residue at 15-minute intervals.

2. Acid feed and dissolver overflow volumes were 0.47 liters at 15-minute intervals.

In all the continuous runs, the vigorous reaction immediately after slag and crucible charging generated large amounts of unstable foam. The foam and reaction subsided in a few minutes, but this presents a significant foam-over problem in the operation of a continuous dissolver. Reducing the amount of solids in a given charge and increasing the frequency of charging should alleviate the foam-over problem.

A solids heel remained at the end of each continuous run. The buildup of an equilibrium heel also was evidenced in the "cold" pilot plant runs on plant-size equipment.(2) The undissolved residue heel encountered in our work was approximately 8 per cent by weight, which is considerably larger than encountered in "cold" pilot plant studies. An improved sparge in our dissolver might have minimized the solids heel buildup.

The developed flow sheet for continuous dissolution of canned slag and crucible is presented in Figure 2.

Dissolution of Residual Dissolver Heel

Attempts were made to dissolve the residual dissolver heel. A 4M HNO_3 or 6M HCl solution were the most successful reagents. Approximately 28 grams of a 50-gram solids batch were dissolved in one liter of 4M HNO_3 in three hours, while 31 grams of a 50-gram batch were dissolved in two hours using one liter of 6M HCl. Other reagents used included 16M HNO_3, 8M HNO_3, 2M HNO_3, 7.5M HNO_3 - 1M HF - 0.3M ANN, and 2M HF. Emission spectrograph analyses of the heel material showed that the main constituents are Al, Mg, Ca, Fe, Zn, and Si. The residual heel did not contain any plutonium. Periodic dissolver cleanout runs using 4M HNO_3 can be used to minimize the amount of residue heel. Any excessive undissolved heel buildup in a dissolver will have to be removed as a solid, checked by neutron count for plutonium, and, according to plutonium content, be discarded or subjected to a lengthy batch dissolution in 4M HNO_3 or 6M HCl.

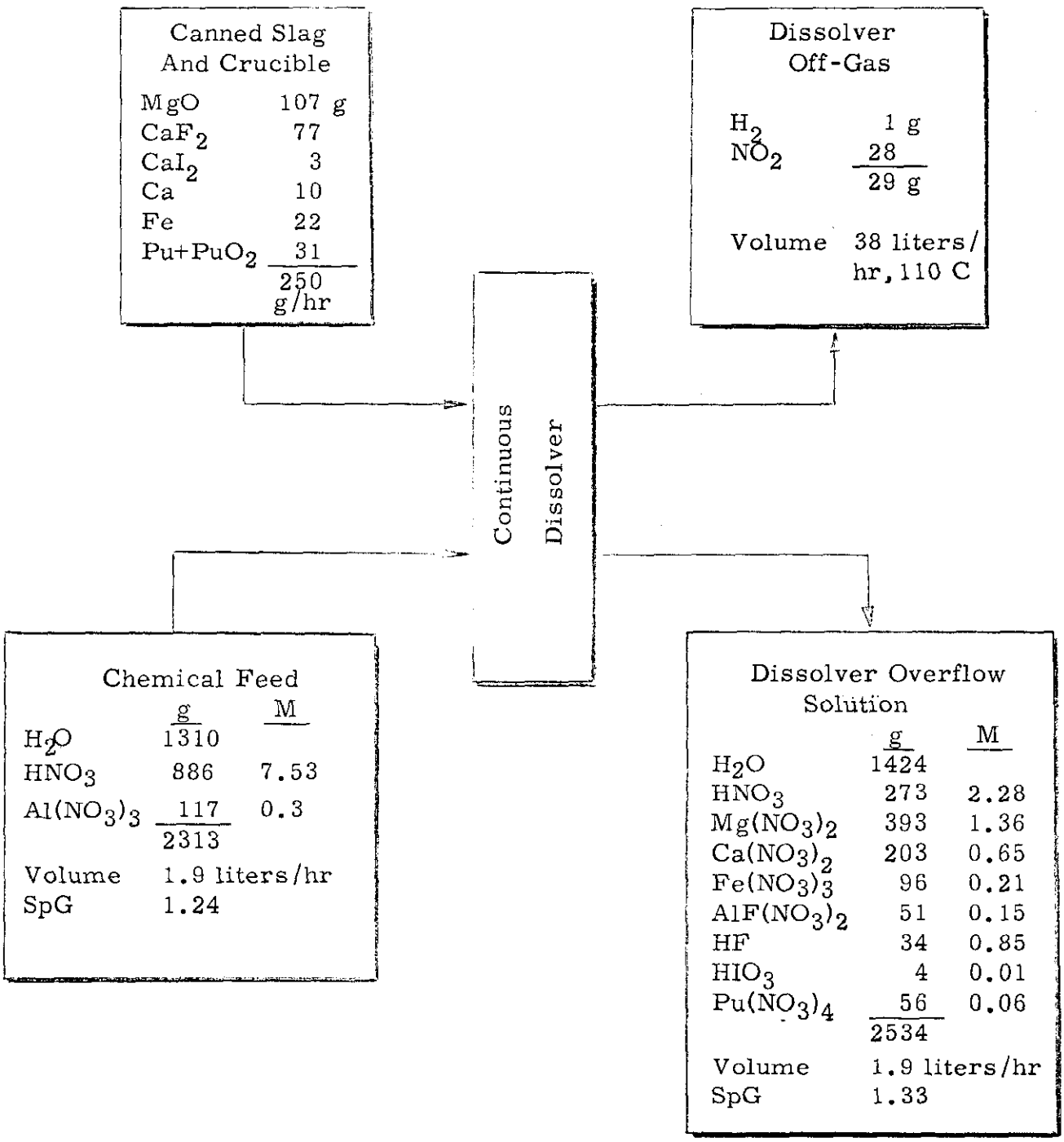

FIGURE 2

CONTINUOUS DISSOLUTION OF PLUTONIUM-BEARING SLAG AND CRUCIBLE RESIDUES (LABORATORY SCALE)

Solubility of Plutonium Iodate

The solubility of plutonium iodate in the dissolver overflow solution was unknown. Insoluble plutonium iodate will not extract, but will go out in the solvent extraction waste stream. Dissolver overflow solution was, therefore, spiked with HIO_3 to determine the minimum concentration of iodate required to precipitate plutonium iodate. A concentration of 27.5 g/l iodate was required to precipitate plutonium iodate from solution. The iodate concentrations in all the continuous dissolver runs were much lower than this value (< 5 g/l iodate). At these concentrations, ~~isoluble~~ insoluble plutonium iodate formation should not be a problem.

Extraction of Plutonium from Slag and Crucible Solutions

Dissolver overflow solution was adjusted to extraction column feed specifications ~~(CAF)~~ and contacted with 20 per cent TBP - 80 per cent CCl_4. Four stages of extraction reduced the plutonium concentration in the aqueous phase from 2 g/l to 0.003 g/l in one CAF sample, and from 0.2 g/l to 0.0005 g/l in another sample. Storage of the solvent extraction feed solution for five days prior to extraction did not inhibit the extractability of the plutonium.

Samples of ~~CAF~~ extraction feed were spiked with 0.1 to 0.3M H_2SO_4 and contacted with 20 per cent TBP - 80 per cent CCl_4. The presence of the sulfate did not affect the extraction of plutonium.

A sample of ~~CAF~~ extraction feed was spiked with 0.08M titanium to determine the effect of that element on plutonium extraction. The presence of titanium did not affect the extractability of plutonium in 20 per cent TBP - 80 per cent CCl_4. The titanium remained in the aqueous phase waste stream.

(2 M HNO_3, 1 M Al^{+3}, 0.6 M Mg^{+2}, 0.3 M Ca^{+2}, 6.1 M NO_3^-

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