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HANFORD ATOMIC PROI

PROPOSED ALTERNATE DISSOLVING FLOWSHEETS FOR THE REDOX PLANT

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by

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INTRODUCTION

Current operation of the Redox plant dissolvers results in evolution of ammonia during the slug jacket removal step. Staggering the schedules of the dissolving cycles of the three dissolvers is being practiced at present to prevent the formation of ammonium nitrate crystals in the stack gases, but this procedure limits the dissolver capacity. Steps are being taken to provide ammonia scrubbers for the dissolvers to eliminate this need for close scheduling of dissolving operations.

It has been proposed (HW-30838) that mercury-catalyzed nitric acid dissolving of the jackets be adapted to the Redox plant. Such a process would eliminate ammonia from the off-gases and would offer several other advantages as well. A flowsheet was proposed based on work in the Process Chemistry laboratory and developed by runs in the 321 Building 1/20-scale dissolver. However, the off-gases resulting from this flowsheet were found to contain hydrogen, and further laboratory work was thus undertaken to provide a solution to this problem.

OBJECTIVE

It is the purpose of this paper to summarize the recent development work on the mercury-catalyzed nitric acid slug de-jacketing and dissolving procedure, and to show how these findings may be applied to the Redox operation by the use of alternate flowsheets.

SUMMARY AND CONCLUSIONS

Recent studies have led to the proposal of three different flowsheets utilizing the mercury-catalyzed reaction of aluminum with nitric acid. All of these flowsheets eliminate ammonia from the off-gases, permit shorter dissolver time cycles, and offer the other previously discussed (HW-30838) advantages of acid jacket removal. The flowsheets are shown in detail in Figure 1 and are compared with the current operation in Table I.

One flowsheet produces hydrogen in the off-gases, but depends on gas treatment to prevent any hazardous conditions from arising. Another flowsheet results in no ammonia or hydrogen formation but requires the use of a jacket removal solution hold-up tank and achieves time economy by neutralizing the excess acid in the dissolved uranium cuts with acid-deficient aluminum nitrate solution produced in jacket dissolving. The third flowsheet also eliminates ammonia and hydrogen and does not require additional vessels other than the rinse tanks, but discards a portion of the coating removal solution. The flowsheets retain their relative advantages when either up-draft or down-draft dissolving techniques are used.

DISCUSSION

A. Summary of Dissolving Studies

The following summary gives the findings of recent laboratory work. A comprehensive report will be prepared later giving the details of this work.

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1. Laboratory-scale mercury catalyzed dissolvings were made using reject un-irradiated Hanford 4-inch slugs with 100% heel of unjacketed metal present. All-glass equipment was used.
2. Hydrogen evolution was detected and followed, and sufficient experience was gained in observing hydrogen evolution to enable confident statements to be made as to the relative quantities evolved in the experiments performed.
3. Several types of dissolving media resulted in peaks of hydrogen concentration in the evolved gases exceeding the lower explosive limit. These peaks lasted from 10 to 60 minutes. Variation of chemical conditions permitted some control of the height, duration, and period of occurrence of these peaks. Since the hydrogen peaks generally coincide with the maximum off-gas evolution rate, cooling the reaction to prevent the dissolver pressure from going positive suppresses the hydrogen peak by slowing the reaction and permitting the dilution of the off-gases with in-leakage air.
4. Hydrogen concentrations greater than the lower explosive limit resulted from solutions of nitric acid (60, 45, or 23%), ANN, and UNH, when the free acid present was over a few per cent by weight.
5. Low hydrogen evolution (less than 1%) resulted from ANN and sodium nitrate solutions when the free acid present was kept very low. This was also found to be the case when water was the starting solution, and means that the acid was continuously added at a rate only slightly exceeding that at which it was consumed, resulting in an instantaneous free acid concentration ranging from 0 to 0.5 M.

B. Summary of Off-Gas Treatment Studies

Studies of means for oxidizing the hydrogen formed by the reaction included limited laboratory work plus literature searches. These studies have disclosed the following information.

1. The use of chemical additives in the reaction vessel resulted in such a great change in the primary aluminum-nitric acid reaction that the effects of these additives on hydrogen evolution could not be studied. One agent, cupric ion, previously found to catalyze hydrogen-oxygen reaction in water was such an effective aluminum-nitric acid poison that it is being considered as a possible "drowning" agent.
2. The use of precious metal catalyst beds for oxidizing the hydrogen in the off-gases is perhaps feasible, but serious complications in handling the operation in the plant would have to be worked out. This process, currently being applied on similar systems elsewhere, is also a possible means of eliminating ammonia from off-gases.

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C. Discussion of Flowsheets

Three flowsheets utilizing mercury-catalyzed dissolving are shown in Figure 1. A summary of pertinent points for comparison of the proposed flowsheets with the current flowsheet is given in Table I; the following discussion is an expansion of the material summarized.

1. Current Operation

- a. Coating Removal - Dissolution of aluminum jackets is in NaNO_3 -NaOH solution, resulting in ammonia in the off-gases. Coating removal solution is sent to stored waste.
- b. Dissolving Cuts - Uranium dissolving is begun by covering the bare slugs with 45% nitric acid, and followed by incremental addition of 60% nitric acid to maintain a constant reaction rate. Dissolving is carried down to slight excess free nitric acid (from 0.05 to 0.2 M). Two cuts are required.
- c. Remarks - The procedure for uranium dissolving cuts has been improved by experimentation in the plant since the start of operations. No significant changes have been made in the coating removal operation, but time saving might possibly be incorporated to decrease the over-all dissolver time cycle by 5 to 10%. The time lost due to the rinse between use of caustic and acid is a definite disadvantage which this procedure has in time cycle comparison with the other procedures presented.
- d. Modifications - In considering other types of flowsheets and their required modifications, it should be apparent that modifications of the current flowsheet might be in order. Thus, if a catalyst bed could be used for hydrogen oxidation as required by Alternate Flowsheet No. 1, the use of NaOH without NaNO_3 for coating removal could be considered. Or, if catalyst beds of any type are considered, then an ammonia removal step might be more attractive than a caustic scrubber since it involves no solution handling and thus results in a simpler initial installation and little operating attention. Likewise, a triple-purpose condenser installation (down-draft condenser-ammonia scrubber-concentrator) would influence the feasibility of this dissolving procedure.

2. Alternate Operation No. 1

- a. Coating Removal-First Cut - Aluminum and uranium dissolution is begun in 45% nitric acid, and this is followed by incremental addition of 60% nitric acid with 5% mercury catalyst present. This results in hydrogen in the off-gases. The solution goes into the process after blending with the second cut.

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- b. Second Dissolving Cut - This dissolving cut is similar to current dissolving cuts, but a larger amount of metal is dissolved.
- c. Remarks - This flowsheet results in the evolution of hydrogen in quantities that consistently approach or exceed the lower explosive limit in the off-gases. Recent laboratory studies have given a better understanding of the nature of this hydrogen evolution. While the chemistry of the flowsheet has been demonstrated on a semi-works scale, the hydrogen picture on that scale is not complete. The catalytic destruction of the hydrogen in the off-gases is possible, but much additional development work is necessary.

The use of this procedure results in two cuts of different composition, requiring some routing of these cuts in the storage tanks to insure a uniform feed composition. The details of such a routing have not been worked out to determine the requirements for equipment scheduling or changes.

- d. Modifications - Since the presence of mercury suppresses iodine evolution during dissolving, it might be possible to eliminate the silver reactors and their electrical preheaters, thus reducing considerably the hazard from potentially high hydrogen concentration before the hydrogen is diluted with the rest of the gases to the stack. Thus perhaps the use of a catalyst bed would not be required. This flowsheet is the result of previous development work, and recent laboratory work with modifications of it has disclosed little advantage to be gained from the standpoint of the hydrogen evolution or other considerations by changing it. Some variation in the rate of incremental acid addition might be indicated, but this could best be developed during plant operation.

3. Alternate Operation No. 2

- a. Coating Removal - The aluminum jackets are dissolved by the catalytic action of 5% mercury in aluminum nitrate solution resulting in a solution of basic aluminum nitrate. This coating removal solution is then used to 1) neutralize and dilute the subsequent uranium cuts, and 2) provide aluminum nitrate solution for the next jacket removal. No ammonia and very little hydrogen (less than 1 volume percent) are present in the resulting off-gases.
- b. Dissolving Cuts - Uranium dissolving follows a procedure similar to current practice, except that the reaction is terminated at a higher free-acid concentration (ca. 1.5 M) resulting in a shorter dissolving time. Two uranium cuts are required.

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- c. Remarks - Time economy is achieved in this procedure by the use of the coating wastes for acid neutralization in the uranium solution thus eliminating the least productive portion of the dissolving cycle. This requires the use of a separate storage tank for the coating wastes, such a tank to be connected to each dissolver for transfer in either direction. One possibility is to use the present H-10 Tank for this purpose. Another possibility is to provide new, larger rinse tanks, since the current use of the rinse tanks is eliminated by acid coating removal flowsheets. The high freezing point of the uranium dissolving cuts will probably require dilution before these cuts are cooled for jetting, thus eliminating possible routings involving the dilution of these cuts at locations other than the dissolver.

The only limits to operation with this flowsheet are heating and condenser capacity, since the reaction may be allowed to proceed as rapidly as possible and will result in no excessive concentrations of hydrogen in the off-gases. Hydrogen evolution from other mercury-catalyzed aluminum dissolvings is a function of high free nitric acid concentration, but a high free nitric acid concentration is possible with this flowsheet only by the accidental use of excess acid in acidifying the basic aluminum nitrate for jacket removal solution preparation.

It was observed in laboratory work that the mercury was insoluble in the acid-deficient aluminum nitrate solution resulting from jacket removal and after the aluminum was dissolved, the mercury was found in pools of the metal in the bottom of the dissolver. If any of this were jetted from the plant dissolvers and storage tanks, part of it would be returned to the dissolver with the coating removal solution, and part would remain in the column feed solution. If it were not removed from the dissolvers by jetting, it would subsequently be dissolved during the uranium cuts, and would essentially quantitatively follow the feed solution to the solvent extraction battery.

- d. Modifications - If storage tank and routing arrangements cannot be worked out, several variations of this process may be considered. The ANN might be used as a coating removal agent on each dissolver cycle, and the resulting material could then go 1) entirely to process, 2) half to process and half to waste, 3) entirely to waste. The material will contain about 1 gram per liter UNH. While discarding all or part of the waste is desirable from the standpoint of reducing the load on the feed preparation steps, including it in the feed solution reduces the first cycle solvent extraction salting strength requirements. While such use of ANN in the feed detracts from back-cycled waste advantages, back-cycled wastes might conceivably be used as the source of ANN for jacket dissolving.

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Another modification might be to use UNH solution from previous dissolving cuts as a replacement for the ANN solution. This procedure is still under investigation in the laboratory, but previous experience has shown that this de-jacketing technique gives hydrogen in the off-gases and that acid-deficient UNH solution result in precipitation of U(IV).

4. Alternate Operation No. 3

- a. Coating Removal - Aluminum jackets are removed by slowly adding 60% HNO_3 to water (containing 5% mercury) in which the slugs are immersed. No objectionable off-gases are produced. Most of the coating removal solution is used (via routing into rinse tanks) for dilution of the dissolving cuts, but some goes to waste.
- b. Dissolving Cuts (2) - Uranium dissolving cuts are similar to current dissolving except that 50% nitric acid is made up by using the coating removal solution.
- c. Remarks - This procedure uses only existing equipment with no changes. While routings of the coating removal solution appear complex, these may easily be expressed in step-by-step procedures. The process produces a waste giving some loss of S-F materials (about 0.03% U, with Pu in proportion) and throws away a usable process chemical, but it does produce a feed of lower aluminum concentration and a somewhat reduced load on the feed preparation step.

The low hydrogen evolution from this procedure is directly related to the rate of nitric acid addition; too rapid nitric acid addition will result in high hydrogen content of the off-gases. The percentage of hydrogen present in the off-gases for this type of flowsheet, is directly related to the total off-gas volume, and an increase in differential pressure across the dissolver tower will serve to warn that the reaction is proceeding too rapidly.

- d. Modifications - Similar coating removal with low hydrogen evolution may be accomplished by using 0.5 to 4.0 M NaNO_3 in water, with incremental acid addition. However, no advantage is seen in such a process to justify the purchase of this agent or the storage of it as a waste component.

A smaller initial volume of coating removal solution could allow all of such solution to be used in the process with none being sent to waste, but requirements for keeping the free nitric acid concentrations low and being able to cover the slugs,

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establish the minimum permissible volume. If a triple-purpose dissolver condenser were used, a solution concentration could be achieved during coating removal that would not exceed solubility limitations and would allow all the coating removal solution to be used in the feed. Likewise, routing the wastes to the back-cycle concentrator for the IA Column scrub solution would use these wastes and prevent S-F material losses.

Waste losses indicated for the proposed flowsheets are based on the uranium dissolved in coating removal. These values were obtained in laboratory studies, with a clean dissolver used for each run. If a dissolver is used for coating removal and dissolver cuts without a rinse between the cuts and the following jacket removal, the jacket solution will contain that uranium and plutonium dissolved during coating removal, plus that retained in the equipment due to surface wetting, non-jettable heels, etc. Thus, if any procedure involving routing of coating wastes to waste is considered for plant application, data on waste losses should be obtained for the sequence of dissolving cuts prior to coating removal, and consideration should be made for possible inclusion of a rinse step prior to jacket removal.

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TABLE I

COMPARISON OF DISSOLVER OPERATION FLOWSHEETS

	Flowsheet		
	Current	Alternate 1	Alternate 2
1. Time Cycles, Hours 1)			
Heating (30 min., ea.)	1.5	1.0	1.5
Cooling (40 min., ea.)	2.0	1.3	2.0
Jetting (30 min., ea.)	1.5	1.0	1.5
Rinsing	1.0	-	-
Coating Removal	6.0	10.0	3.0
First Uranium Cut	8.0		6.5
Second Uranium Cut	8.0	10.0	6.5
Total	28.0	23.3	21.0
2. Buff-Gases			
a. Troublesome agents	NH ₃	H ₂	None
b. Required action	Scrubber	Modification	None
3. Coating Waste Losses	Current	None	None
4. Vessel changes	None	None	Storage Tank
5. Routings			
Coating Removal	No change	None	Simple changes
Cuts	No change	Required	No change
6. Storage Tank Solutions			
U, M	2.6	2.0	2.0
Al, M	0.0	0.58	0.4
HNO ₃ , M	0.1	0.0	0.2
Sp. Gr.	1.830	1.727	1.705
Freezing Point, °C.	25	25	20
Relative Volume	2910	3780	3755
			3760

Notes:

1) Does not include charging time, which would be the same for all procedures.

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FIGURE 1

ALTERNATE DISSOLVING FLOWSHEETS

Basis: One 4-inch slug (4 lbs. U, 58 g. Al), 100% heel. All volumes in milliliters.

ALTERNATE NUMBER 1

ALTERNATE NUMBER 2

END

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