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Post Office Box X
Oak Ridge, Tennessee

ORNL
CENTRAL FILES NUMBER
58-11-106

COPY NO. 67

DATE: November 19, 1958

SUBJECT: Development of Batchwise and Semi-Continuous Darex Flowsheets Using 61 Wt. Per Cent HNO_3

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ABSTRACT

Both batch-wise and semi-continuous Darex flowsheets were developed on a 1.4 liter scale using 61 weight per cent nitric acid to volatilize and/or decompose chloride. The 61 per cent acid is favored over higher concentrations for safety and availability. The batch flowsheet features simplicity and ease of operation; either batch or continuous dissolution can be used. The semi-continuous scheme, which assumes continuous dissolution, offers reduced cycle times but more complex operation. Both flowsheets accomplish chloride removal to < 350 ppm by adding batch-wise only the amount of nitric required for solvent extraction feed adjustment and regeneration of dissolvent.

DISCLAIMER

The purpose of the Darex Process is to convert SS-U and SS-UO_2 fuels into chloride-free nitrate solutions suitable for processing in existing solvent extraction equipment. Chloride is necessary to effect dissolution of SS in HNO_3 but must be removed to avoid corrosion of feed adjustment, solvent extraction and waste handling equipment.

Darex consists basically of three steps: (1) dissolution, (2) chloride removal, and (3) solvent extraction feed adjustment. These steps may be accomplished continuously, semi-continuously, or batchwise using nitric acid solutions from 61 to 95 wt % HNO_3 to volatilize and/or decompose the chloride. Since the proposed Darex head-end in the PRFR pilot plant is to operate batch-wise or semi-continuously, and since safety precludes the use of 95% HNO_3, flowsheets were developed to use the readily available 61% HNO_3 in both batch-wise and semi-continuous schemes.

Batch-wise Flowsheet - The advantages of the batch flowsheet are simplicity and ease of operation. All steps are purely batch-wise with no controlled continuous additions or withdrawals required. There is no recycle of radioactive, chloride containing HNO_3 except to the dissolution step where it is completely utilized in the next batch. The HNO_3 added to accomplish chloride removal is only that amount necessary to provide solvent extraction feed (3 M in HNO_3) and to regenerate dissolvent for the following batch. The batch flowsheet assumes as starting point the entire batch of dissolution product (DP) to be processed. Therefore, it does not matter whether the DP was generated in a batch or continuous dissolution.

A minimum equipment flowsheet for such a process is shown in Figure 1. Necessary equipment includes a dissolver, chloride removal and feed adjustment vessel, two condensers, a waste hold tank and two aqua regia tanks. Only one aqua regia tank would be required if immediate hydrogen ion and chloride analyses could be assumed. Operation would be accomplished by first charging a batch of DP to the chloride removal vessel and then removing a waste cut (< 1.0 M in total acid) to the waste hold tank. A HNO_3 addition is made to increase chloride volatility and the first mixed acid cut is collected in the mixed acid catch tank; this cut contains about one-half the chloride present in the DP. It is at this point that the metals concentration is the highest and the volume the lowest (about 21.4% of DP). Another HNO_3 addition is made and reflux is carried out to decompose the remaining chloride. The chloride free (< 350 ppm) product is boiled to remove excess HNO_3, and this cut is combined with the first mixed acid cut and adjusted to 5 M HNO_3-2 M HCl in a volume equal or less than the original dissolvent volume. Only H_2O dilution of the metals containing solution is required to produce solvent extraction feed.

The waste cut (< 1.0 M hydrogen ion) mentioned earlier could be treated with excess caustic and used as the liquid in the off-gas scrubbing tower (not shown in the flowsheet). This procedure would minimize the volume of the chloride containing radioactive waste stream.

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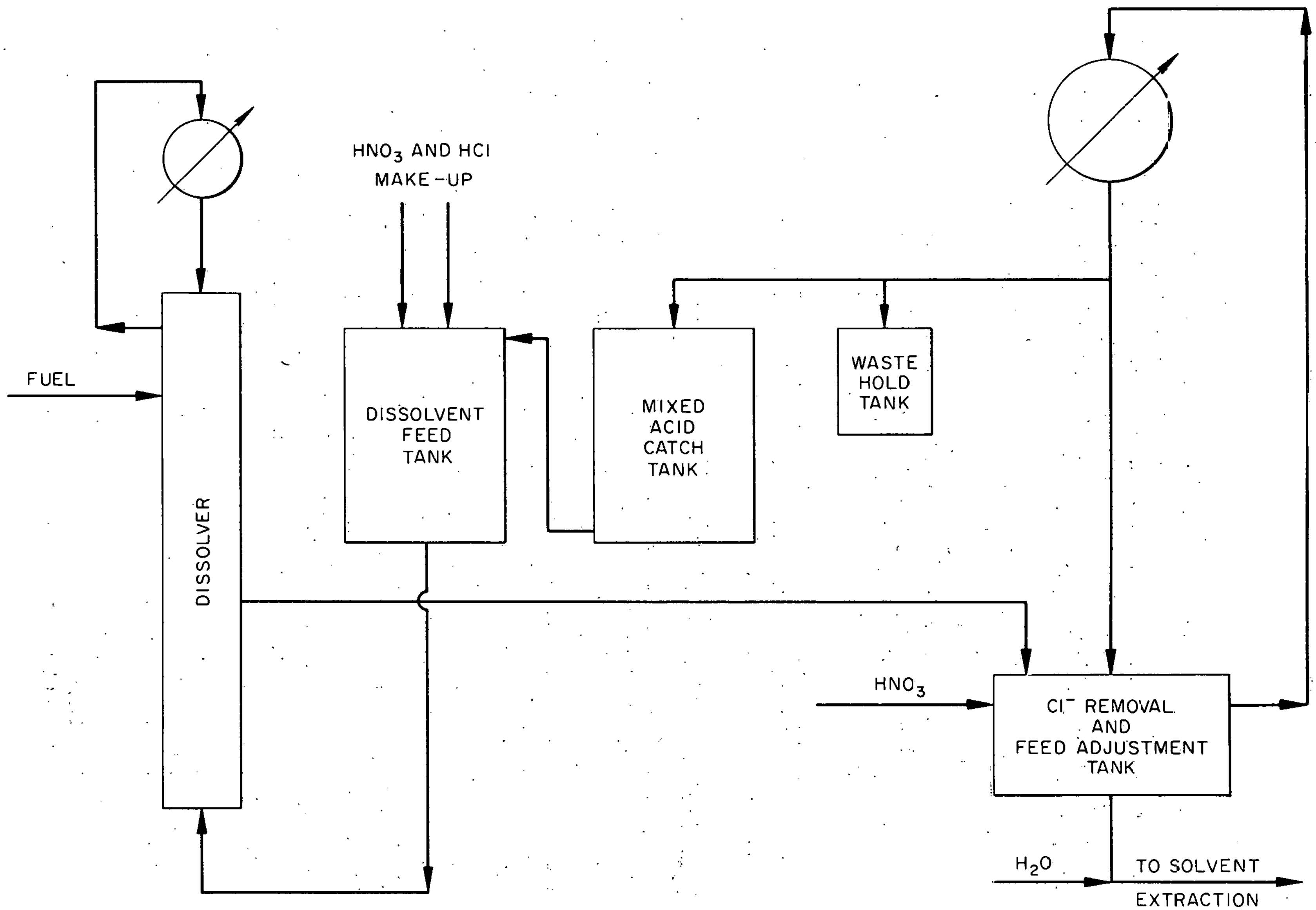

Fig. 1. Equipment for Batchwise or Semi-Continuous Darex Using 61 wt% HNO_3.

The laboratory work on which the flowsheet is based was performed using 1400 cc batches of DP produced by dissolving prototype APPR elements (~ 10% depleted U) to 62 g metal/liter in 5 M HNO_3-2 M HCl. A material balance showing the volumes and compositions of the side streams and the metals containing product at key points during the process is shown in Figure 2. The laboratory procedure was as follows:

1. Charge 1400 cc DP to 2 liter boiling flask.
2. Boil off 300 cc to waste.
3. Add 300 cc 61% HNO_3 - begin air sponge at ~ 1/4 SCFH.
4. Boil off mixed acid (~ 1050 cc) until volume of product = ~ 300 cc.
5. Add 600 cc 61% HNO_3 and reflux for two hours.
6. Boil off 220 cc mixed acid (HNO_3 with trace chloride).
7. Dilute to 1600 cc solvent extraction feed.

It was necessary to use a gas sparge in order to remove the necessary HCl in the first mixed acid cut. Only O_2 and air were tried and appeared equally effective.

<u>Semi-Continuous Flowsheet</u> - The semi-continuous flowsheet has the advantages of a smaller chloride removal vessel and time savings made possible by allowing the chloride removal step to begin after the dissolution has been only partially completed. This procedure assumes a dissolver which operates continuously with respect to the liquid phase; the aqua regia is fed and dissolution product is removed continuously with a small constant hold-up in the dissolver. The remainder of the equipment is the same as that shown in Figure 1. Fuel is charged batch-wise to the dissolver; dissolvent is fed continuously; dissolution product flows into the chloride removal and feed adjustment vessel. When the desired level is reached in this vessel, heat is applied and a waste cut is boiled off (at the same rate as the DP addition) to the waste hold tank. When the desired waste volume has been collected, a batch-wise HNO_3 addition is made and the overhead condensate is redirected into the mixed acid catch tank. The chloride is volatilized during this step and the mixed acid collection is continued until the desired low volume remains in the feed adjustment vessel. (The dissolution would be completed less than half-way through the mixed acid boil-off). From this low-volume point the flowsheet is identical to the batch-wise flowsheet.

The laboratory work was done with 1400 cc batches of DP metered to the chloride removal vessel to simulate the discharge of a continuous dissolver. The procedure was as follows:

1. Change 700 cc DP to 2 liter boiling flask.
2. Continuously add 300 cc DP while removing 300 cc to waste.
3. Add 300 cc 61% HNO_3 batch-wise and begin air sparge.

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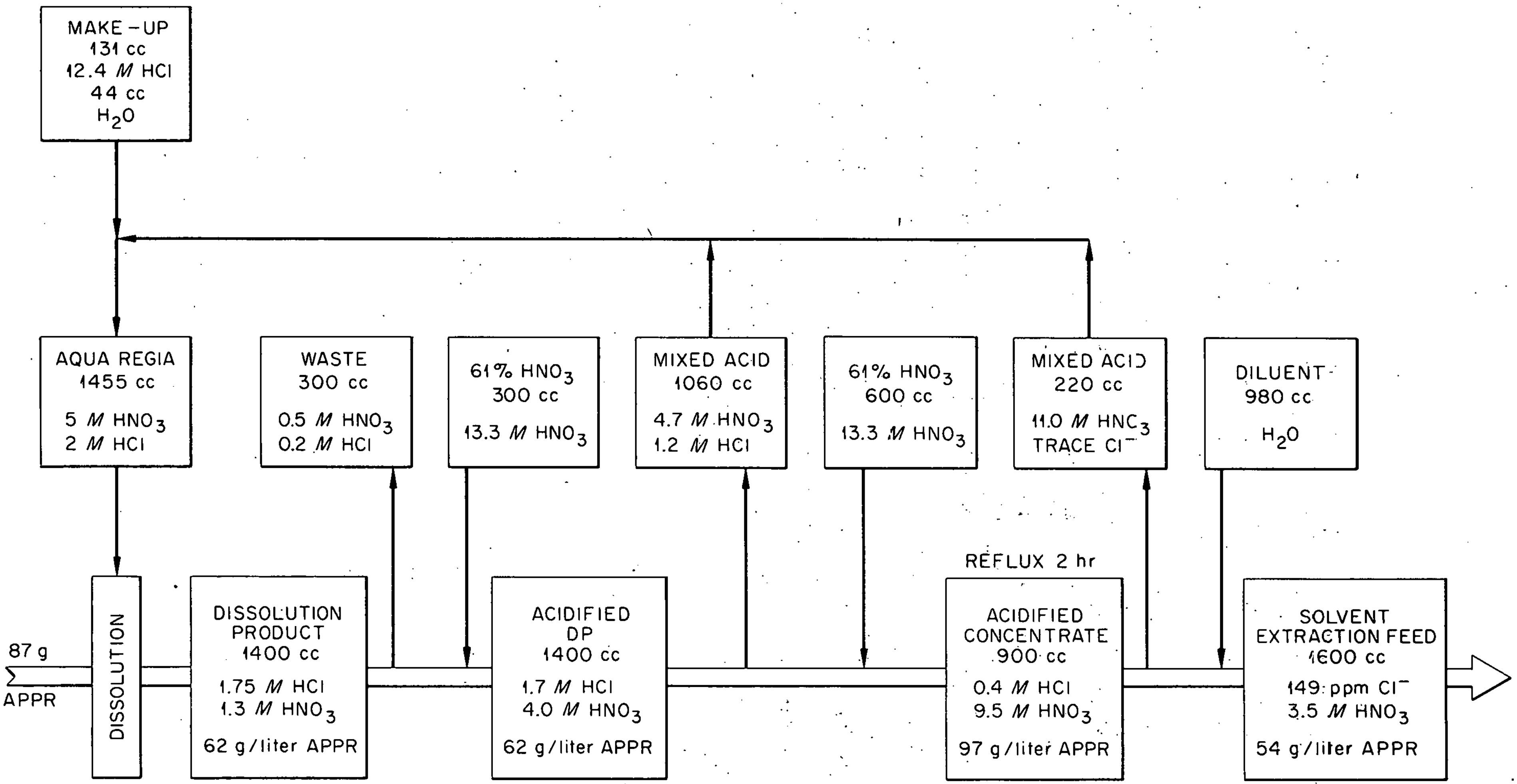

Fig. 2. Material Balance for Batchwise Operation Using 61 wt% HNO_3.

4. Continuously add the remaining 400 cc DP while removing 400 cc mixed acid and continue to remove mixed acid until volume of concentrate is reduced to ~ 300 cc.
5. Add 600 cc 61% HNO_3 and reflux 2 hours.
6. Boil off 250 cc mixed acid (HNO_3 with a trace of chloride).
7. Dilute to 1600 cc solvent extraction feed.

Since the amount of DP and 61% HNO_3 additions are the same in both cases the material balance for semi-continuous operation is very similar to that for batch operation (see Figure 3). The waste cut here is slightly more concentrated (~ 1.0 M hydrogen ion) and the first mixed acid cut is slightly weaker in HNO_3. Apparently, there is a little more loss due to decomposition in the semi-continuous system. From the second HNO_3 addition on through the preparation of solvent extraction feed the steps are the same with slight variations in volumes and compositions.

These flowsheets are not presented as carefully worked out optimizations and indeed require further adjustments and polishing, but they do show that Darex is a flexible process. They also serve to illustrate the principle that chloride can be removed to the specified < 350 ppm by the judicious application of only that amount of HNO_3 required for solvent extraction feed adjustment and for the regeneration of dissolvent for the next batch.

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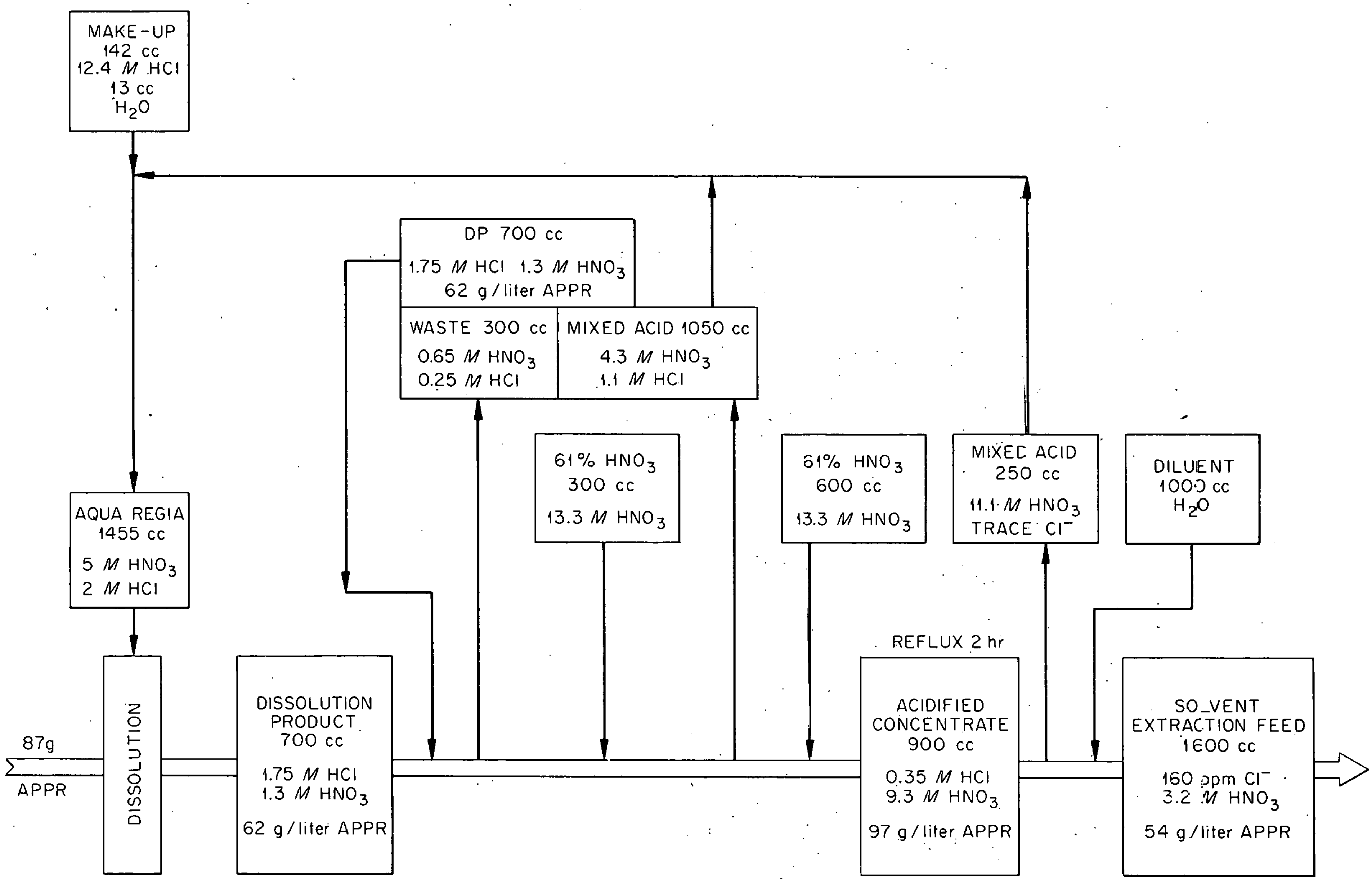

Fig. 3. Material Balance for Semi-Continuous Operation Using 61 wt% HNO_3.

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