OAK RIDGE NATIONAL LABORATORY

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UNION CARBIDE CORPORATION

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U.S. ATOMIC ENERGY COMMISSION

ORNL-TM-568

COPY NO. - 2

DATE - April 24, 1963

REMOVAL OF MERCURY FROM WASTE SOLUTIONS PRIOR TO CALCINATION OR FIXATION

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ABSTRACT

More than 99.9% of the mercury was removed from Hanford 1965 FTW waste by displacement with copper. The method appears to be quite feasible for all except the more concentrated of the nitrate wastes.

An evaluation of the advantages and disadvantages of the method compared to the operation of a mercury trap in the calciner off-gas line is desirable.

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1.0 INTRODUCTION

Mercury cannot be quantitatively retained in the solid product obtained by calcination-fixation of waste because it forms no compounds which are stable at high temperatures. Attempts to operate a mercury trap in the off-gas line from the fixation pot have been successful in trapping a maximum of about 50% of the total mercury present on both laboratory and unit operations scales. In batch operations it will probably be possible to hold the top of the fixation pot at a relatively low temperature until the final calcination step and then to trap out most of the mercury together with a fraction of rather concentrated nitric acid. This side stream would presumably be sent to a separate waste storage tank for eventual reprocessing in a special campaign. This procedure, while feasible, appears to be unduly cumbersome, and limits the operation of the system to a true batch process. Removal of the mercury from the feed to the evaporation-fixation system appears preferable if it can be accomplished simply and cheaply.

2.0 POSSIBLE METHODS OF REMOVING MERCURY DIRECTLY FROM THE WASTE STREAM

It is technically feasible to remove mercury from the waste before the latter reaches the feed tank for the evaporation-fixation process. The following methods of separation have been considered:

a. Solvent extraction with organic sulfide solvents as suggested by W. H. Baldwin.[1] In addition to extra solvent extraction equipment this would require fairly extensive studies to determine the amounts of fission products removed, development of solvent recovery procedures and very probably studies of solvent degradation, and would certainly result in the inclusion of at least small amounts of solvent in the feed. It has not been investigated in the laboratory.

b. Removal by precipitation as sulfide. Mercuric sulfide is among the most acid-insoluble of all sulfides with a solubility product of 4×10^{-53}. It should, therefore, displace almost any other metal from a sulfide compound. Ideally this would be accomplished by passing the waste through a column packed with some other acid-insoluble sulfide

with a higher solubility product (e.g. CuS, $K_{sp} = 8.5 \times 10^{-45}$). If equilibrium could be attained complete removal of the mercury would result. Relatively cheap mineral forms of CuS would ideally be employed. There would doubtless be some contamination of the sulfide by other fission products, particularly ruthenium, rhodium and antimony. This concept has not been tested in the laboratory due to the lack of a readily available copper sulfide ore. There is a possibility that chalcopyrite ($CuFeS_2$) might be useable. This has been found to remove a fairly large fraction of ruthenium from waste solutions of other types.[2] Ferrous sulfide was tried but, as expected, it caused excessive gassing with consequent entrainment resulting in removal of only about 80% of the mercury.

c. Electrolysis

Controlled potential electrolysis using a mercury cathode would in theory result in complete removal of the mercury as well as any metals with more positive deposition potentials (e.g. palladium, rhodium, some ruthenium). In practice it would probably be difficult to assure close control of the cathode potential and sufficient contact area and time to assure complete removal without obtaining either entrainment or redissolution of the mercury. If one were to use mercury at all, a better way would be to circulate an amalgam of some metal of the activity required to hold the potential in the desired range.

d. Displacement by a More Active Metal

The position of mercury in the E.M.F. series makes possible its displacement by any of the common industrial metals. Using any combination of standard potentials of Hg^{+2} and Hg^{2++} it can be shown that greater than 99.9% of the mercury should be removable by equilibrium with metallic copper or with any more active metal. This concept has been subjected to scoping studies in the laboratory.

3.0 LABORATORY TESTS

Initial tests consisted in contacting 5 grams of the active metal with 100 ml of simulated Hanford 1965 FTW waste solution* for 30 minutes in a beaker with occasional stirring. Filtration and analysis of the

* Composition (g moles/l): H^+-0.5, Na^+-0.30, Al^{+3}-0.05, Fe^{+3}-0.10, Cr^{+3}-0.02, Ni^{+2}-0.01, SO_4^{-2}-0.15, PO_4^{-3}-0.005 SiO_3^{-2}-0.01, F^--0.02, Hg^{+2}-0.0035, Ru-0.002, NO_3^- to balance.

filtrate indicated 96% removal of the mercury from solution in the beakers where copper turnings or steel wool had been employed, 65% with mossy tin, 41% with granulated zinc and 60% with aluminum pellets. The lower percentages of removal with tin, zinc and aluminum were doubtless due to non-attainment of equilibrium due to the relatively smaller contact area of these metals. Only the filtrate from the steel wool was tested for ruthenium removal. Eighty to ninety-five percent of the ruthenium had been removed in this case.

Experiments were carried out in which the waste solution spiked with 0.1 μc/ml of Hg^{203} was passed through glass columns packed with steel wool and a mixture of copper turnings and copper shot, respectively. Column residence times were about 35 minutes in each case. The steel wool removed greater than 99% of the mercury for the first 14 column volumes, after which the column virtually ceased to function due to channeling caused by dissolution of the steel wool. The column packed with copper removed $\geq$ 99.9% of the activity during the passage of approximately 50 bed volumes at which time the experiment was arbitrarily ended. At the time of cessation about one-ninth of the lower part of the column had been disintegrated due to amalgamation and acid attack. There was little if any gassing during column operation and no appreciable increase in the activity of the effluent had been observed. Copper in the column effluent analyzed 0.054 M (3.45 mg/ml), four times more than the stoichiometric amount required for displacement of mercury according to the equation:

$$Hg^{+2} + Cu \rightleftharpoons Hg\downarrow + Cu^{+2} .$$

Since the minimum residence time for quantitative displacement has not been determined it is highly probable that the amount of copper dissolved can be appreciably diminished by use of a shorter residence time. Unless the solution were de-aerated, however, it is not likely that the copper dissolved can be reduced to a value closely approaching the theoretically minimum amount.

In a test run using "Acid-killed Purex waste" solution* the column soon became plugged, apparently with copper sulfate, and the effluent was very blue with dissolved copper. Rather obviously the method will be more practical if performed on the original waste rather than on the evaporator bottoms.

* Composition (g moles/liter): H^+-0.3, Na^+-1.2, Al-0.2, Fe^{+3}-1.0, Cr^{+3}-0.02, Ni^{+2}-0.02, SO_4^{-2}-2.0, Hg^{+2}-0.013, NO_3^- to balance.

4.0 CONCLUSIONS AND RECOMMENDATIONS

Removal of 99% of the mercury from Hanford 1965 FTW waste solution prior to fixation appears feasible. Such removal does not appear to be unduly difficult or expensive.

The removal step would take place in a column consisting essentially of an enlarged section of pipe located between the waste storage tank and the feed tank for the fixation process (Fig. 1). The bed, consisting of metal pellets or shot, would be supported on a plate with perforations of a size such as to allow the liquid mercury to drip through into an annular sump surrounding the intake pipe. As the metal in the lower part of the bed became degraded in size the bed would settle and more metal would be fed in from the loading chute. Mercury collected in the sump would be removed either intermittently or at a very slow constant rate. It could be either stored indefinitely in a very small volume or could be decontaminated (e.g. by vacuum distillation) for re-use.

The use of copper in the column should have the advantage of removing only very small amounts of fission products other than ruthenium, rhodium, and palladium; use of the more active metals (e.g. tin, aluminum, zinc or iron) would considerably increase the number of fission products which might be displaced with the mercury in appreciable amounts. With copper minimum amounts of all fission products can be expected in the mercury due to entrainment in the aqueous solution and adsorption of some of the fission products.

Iron, though considerably cheaper than copper, has the disadvantage of being sufficiently active to react fairly rapidly with even dilute nitric acid with visible evolution of gas. A second disadvantage is that it does not amalgamate with mercury. Lead, which might otherwise be useful, forms an insoluble sulfate which would tend to plug the column if the waste contained appreciable concentrations of sulfate.

Future testing should include a determination of the feasibility of the "dissolving bed" concept (Fig. 1), and determinations of the amounts of ruthenium and other fission products removed with the mercury, optimum residence times for solution in the column, the excess amount of copper dissolved above that required for replacement of mercury, the probable increase in this excess with wastes of higher acidity and the probable effects of radiolysis.

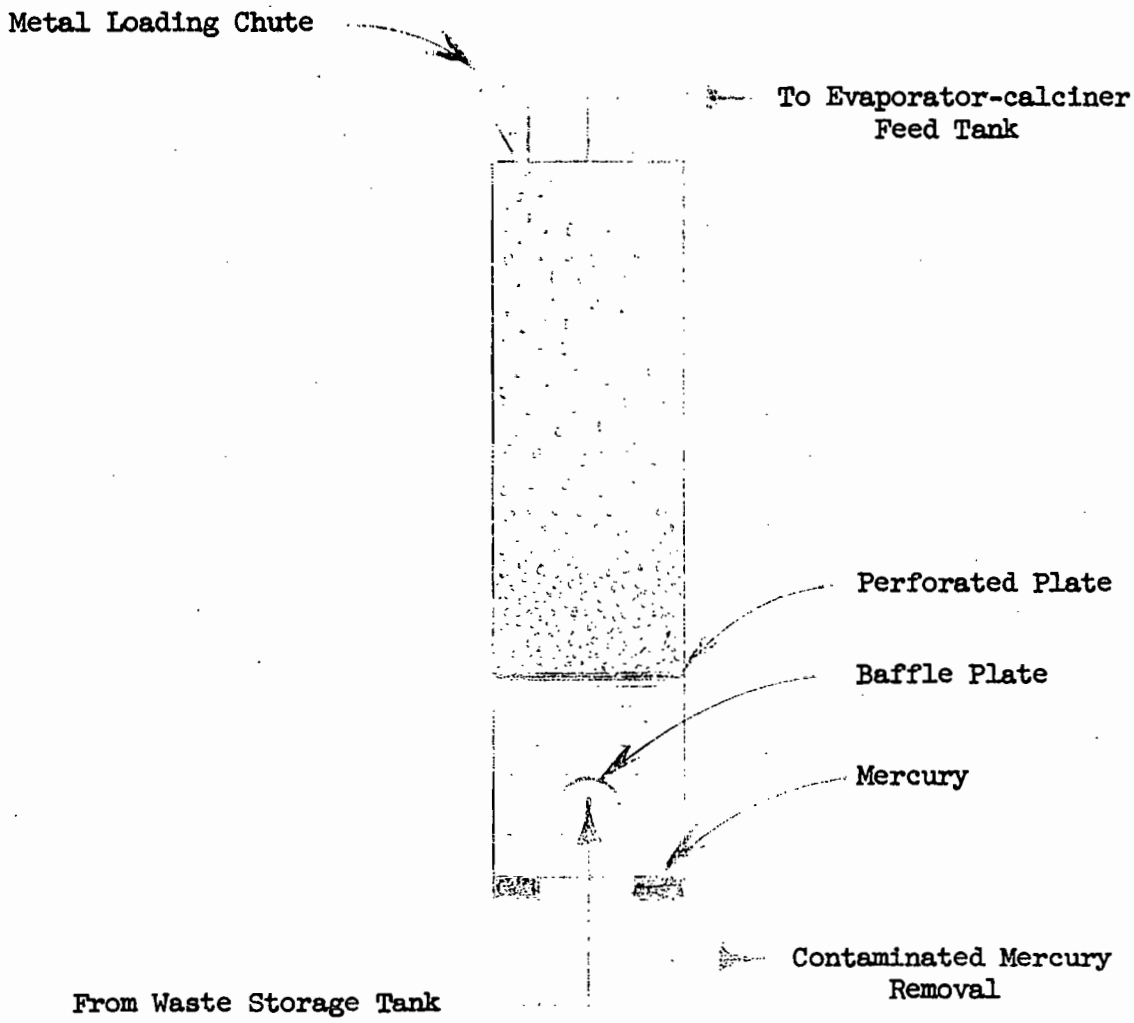

Fig. 1. Schematic diagram of proposed column for continuous removal of mercury from acid waste solutions.

5.0 REFERENCES

1. W. H. Baldwin, ORNL, private communication to W. E. Clark.

2. A. L. Mohan, D. G. Jacobs and E. G. Struxness, "Ruthenium Sorption by Minerals," ORNL-TM-329, August 31, 1962.

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