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REPORT ON A TRIP TO ARGONNE NATIONAL LABORATORY AND OAK RIDGE NATIONAL LABORATORY MARCH 22 - 27, 1948

The purpose of the trip was threefold. The first objective was to discuss with Dr. H. H. Hyman of the Argonne National Laboratory his early work on processes for the recovery of uranium from bismuth phosphate process metal waste solutions. The second objective was to discuss with Dr. Frank Hurd, Sylvan Cromer and other members of the Oak Ridge National Laboratory together with various representatives of the Kellex Corporation and of the Atomic Energy Commission plans for the sampling of the sludges in the program for the study of uranium recovery from such tanks. The third objective was to review with Dr. Frank Hurd the progress made to date by, and future plans of, the Carbide and Carbon Chemicals Corporation toward the development of a process for that recovery.

I. At Argonne National Laboratory

A. With Dr. Hyman, discussion centered around the report PA 29, prepared for the P.P.R., which is in the nature of a summary of his early work on uranium recovery (CN-1953, 2287, 2414). Hyman has re-emphasized the apparent adequacy of his three-step proposal to obtain the necessary decontamination factor of 10^4.

The process in outline is as follows:

Step 1. Scavenging from the alkaline carbonate solution is carried out using as carrier either an inert material added as such or the precipitate obtained by the addition of certain soluble metal salts. Among the latter are the nitrates of Ca, Ba, Fe(II), Mn, and Mg. Of the several materials

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tried, a tilanated silica gel (52% TiO_2, 48% SiO_2) was found to be the best. Its effectiveness was enhanced by the simultaneous addition of $Ca(NO_3)_2$. Under the best experimental conditions found, however, the γ D. F. was only about 20. Decreasing the $CO_3^=$ concentration by the addition of too large an amount of Ca^{++} caused some precipitation of uranium itself. It may be significant, however, that the best decontaminations were obtained in just such cases; perhaps a promising method for the decontamination of such solutions is the partial precipitation of the uranium under similar conditions.*

The principal disadvantages of this step appear to be (a) that large amounts of the expensive gel are required (ca. 1 g/g U) and (b) that decontamination factors are low.

Step 2. Precipitation of the uranium either directly from the scavenged carbonate solution, or from anacidic solution prepared from it, comprises the second step. Precipitating agents tried were NaOH, acetic or formic acid, and H_2O_2. Phosphate and sulfate were carried to by far the least extent in the caustic precipitation (15.5 and 1.0%, respectively); the formic acid precipitation yielded a much denser and faster-settling precipitate than did the acetic acid. The acetic acid procedure gives a better D. F. than the others and is preferred by Hyman for that reason although the precipitate carries 83 and 2.9%, respectively, of the phosphate and sulfate originally present; for the single step, D. F. = ca. 5 or 6; over-all D. F. through Step 2 = >100. Using a long digestion time for Step 1 followed by a formic acid precipitation, an over-all D. F. of >250 may probably be obtained.

The principal disadvantages of this step, and of any uranium-precipitating step, appear to be (a) the fact that great centrifuge capacity would be required and (b) that residual solution volumes are great.

Step 3. The third step consists of a solvent extraction carried out on the solution resulting from the dissolution of the Step 2 precipitate in the minimum amount of concentrated HNO_3. The feed solution used by Hyman is 2 N HNO_3, 3 - 5 N $Al(NO_3)_3$, 15 - 20% UNH. Dibutyl carbitol has been used, diluted with hexone or ether to improve the physical properties without decreasing extractive capacity. The phosphate and sulfate residual in the feed are claimed not to be deleterious to good metal recovery at the aluminum nitrate concentrations used.

Using batch extraction into the solvent and thence again to water gives γ D. F. of ca. 100, 2500, and up to 9000 for one, two, and three cycles, respectively. Over-all D. F. for the three steps is ca. 10^4.

Principal disadvantages of the three-step process as outlined are the necessity of new construction for the solvent-extraction step and the inadequacy of present centrifuge capacity to care for the large volumes of uranium precipitate called for in Step 2 if large immediate production is desired. Furthermore, far from concentrating the fission products into a small volume, the residual solutions from such process would be probably twice the original volume.

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* This is, of course, borne out by the great activity of the sludges in the Hanford storage tanks as compared to that in the supernates.

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B. The opportunity of visiting the Argonne National Laboratory was also used for the purpose of viewing remote-control laboratory equipment of value in carrying out high-level β and γ radiochemistry. R. C. Goertz and members of his group demonstrated extremely versatile motorized manipulators, mirror periscope with quite wide binocular vision, and remotely-operated apparatus, including Chainomatic balance, pipet-control capable of delivering known exact volumes and ring-stand. Remotely-operated can-opener, drill press, and milling machine have apparently been constructed there.

II. At Oak Ridge National Laboratory, K25 Division

A. General Meeting re: Sampling of Metal Waste Tanks

Attendance: J. H. Hayner (A.E.C., Washington); A. Armstrong, D. W. Pearce (Richland); J. G. Beckerley, L. W. Burns (New York); R. W. Cook, J. C. Robinson, H. Roth (Oak Ridge); W. H. Bain, A. Weber, G. Vincent, G. White, Jr. (Kellex Corporation); F. W. Hurd, J. L. Waters, S. Cromer (Carbide and Carbon Chemicals Corporation).

Supernate Sample. The sample of supernatant liquor withdrawn from the Hanford 241 Bldg., 103T tank, on February 6, 1948, has been stored at the K25 Division. A sampler of 1/8 inch pipe for withdrawing portions of the liquor from 1 ml to 1 liter in volume has been devised and used; the equipment is essentially a syphon.

No analysis of this supernate has yet been made but a request to the A.E.C. that a complete F. P. analysis be done by Clinton Laboratories will be made by Carbide and Carbon Chemicals Corporation.

Total β and γ activities of the supernate sample as measured by Carbide and Carbon Chemicals Corporation were stated to agree quite well with those presented in the report by J. B. Work (HW-8697, 1/18/48).

Sludge Samples. Mr. White presented the Kellex proposals regarding the taking of sludge samples from the 101, 102, 103 T tanks at Hanford. The maximum program called for 35 samples in various parts of the 3-tank cascade and the minimum program for 5 samples. The present writer agreed that the suggested minimum program seemed entirely reasonable and stated that he felt certain of the full cooperation of the General Electric Company in it.

It was decided that permission of the A.E.C. be requested for the taking of four sludge samples:

(1) a core sample near the inlet to tank 101T.
(2) a grab sample near the outlet from tank 101T.
(3) a grab sample near the inlet to tank 102T.
(4) a grab sample near the outlet from tank 102T.

It was felt that stratification is not probable in the 102T tank and that grab samples would be representative.

While stratification within the supernates is not expected, it is planned by Carbide and Carbon Chemicals Corporation to construct a plumb-bob to be used in a survey of the supernates against this possibility and also to detect the sludge level in 101 and 102 T.

Following the request of Mr. W. K. MacCready, the present writer re-emphasized the hazard involved in the sampling program and requested that drawings of the sampling equipment be forwarded to General Electric for thorough study, construction in our shops, and try-out by our personnel. It was made clear that, while we were eminently satisfied with the equipment constructed by Carbide and Carbon Chemicals Corporation for the supernate sampling in February, we felt we were fortunate that the operation proceeded so smoothly, and that we approached the sludge sampling with a great deal more trepidation for our personnel. A period of sixty days after receipt of the drawings for construction and try-out of the equipment was requested. Mr. Leo Waters felt that the equipment should be constructed in the Carbide and Carbon Chemicals Corporation shops and tested at Oak Ridge, and the present writer agreed that this was reasonable and very satisfactory to General Electric provided it was realized that we should not be committed by such try-out. The understanding of our position is quite clear.

Carbide and Carbon Chemicals Corporation will therefore proceed further with their design of equipment and expect to have design and construction of core sampler, grab sampler, and plumb-bob completed in thirty days. The prints of the equipment will be forwarded to us upon completion and the equipment itself as soon thereafter as Carbide and Carbon Chemicals Corporation feels that the various pieces are satisfactory.

The present design of a core sampler was discussed with Carbide and Carbon Chemicals Corporation representatives and drawings examined. It is essentially a stainless steel tube, open at the top, probably 5' long by 1/2" diameter and carrying on its upper portion a sliding 10-pound collar confined by upper and lower shoulders on the tube to a slide distance of about 6". The total weight is about 25 pounds. The heavy collar is designed to be raised and then allowed to fall free, as a pile driver in effect, so as to drive the core sampler through the sludge to the bottom of the tank. A bottom closure is provided, to retain the sample on withdrawal of the sampler from the sludge, consisting of thin and flexible overlapping stainless steel sheets, willow-leaf in shape and size, fastened by their bases around the inner circumference of the tube about 1/2 - 1" from the bottom. The willow leaves point centrally into the tube and overlap to form a seal when they are in the closed position; they are forced open by the entering sludge. The whole sampler is to be suspended by means of a bail on the heavy collar from a cable marked in feet and inches so as to provide knowledge of the position of the sampler at any time and so as to control the distance of motion of the pile-driving collar when the sampler has penetrated the heavy sludge.

The filled sampler will be withdrawn through a housing collar at the tank portal and will there by washed with sodium bi-carbonate solution for partial decontamination of its surface. It will then be dropped into a heavy cylindrical container with double gasket at the bottom. Pressure applied to the sampler by a screw-cap lid on the cylinder will force the cutting edge of the sampler through the upper (soft) gasket and into the lower (hard) one effecting a seal. The whole piece will then be packed in [redacted] thus minimizing mixing of the sample during transportation.

Carbide and Carbon Chemicals Corporation hopes to have ready in eleven weeks a sufficiently large part of their new high-level laboratory building so that work on the sludge and liter-scale work on the supernate may be started.

Recommendations Regarding Storage Tanks under Construction. It was felt by the meeting that certain modifications might be introduced into the present design of the metal waste storage tanks, and incorporated into any new construction, so as to facilitate the removal and/or processing of the wastes when the occasion arises. It was not known how far advanced is the presently-proceeding construction of tanks but both Kellex and Carbide and Carbon Chemicals Corporation felt that the following modifications would be desirable in new storage tanks and might still be incorporated in tanks now being installed:

(1) More and larger openings at the top.
(2) Built-in sampling devices.
(3) Piping for pumping out.
(4) Stainless steel or other chemically-resistant lining.

Of these modifications only the first seemed to have a reasonable chance of adoption, since no one is now prepared to recommend a design for sampling devices, since piping installed with the tank might soon be unfit for use due to clogging, and since the use of stainless steel liners seems to be prohibited by high cost.

It was hoped that the tanks now about to be installed might be fitted with five forty-two-inch openings at the top, one at the center and the others located toward the circumference on diameters mutually at right angles and with the outer edges of the openings 15' from the edge of the tank.

B. Carbide and Carbon Chemicals Corporation Processes now under Investigation

1. **Three-step Process.** The Carbide and Carbon Chemicals Corporation three-step process, upon which most of their attention has so far been placed, and which they favor over the others to be described, consists of (a) the phosphate precipitation-scavenging step, (b) the uranium precipitation, and (c) the solvent extraction.

Mr. J. C. Barton, with associates and assistants, is concerned with this work.

Step 1. The alkaline carbonate supernate solution is treated with ferric sulfate; ferric phosphate precipitates. There is some F. P. removal and some carrying down of uranium. The precipitate is centrifuged out and washed with 2% sodium bicarbonate solution which removes the uranium and also some of the F. P. elements from the precipitate. Ruthenium is carried in part by the $FePO_4$ precipitate. There is some evidence that ruthenium in these carbonate solutions is about one-half each Ru(III) and RuO_4.

Step 2. From the phosphate-free and somewhat decontaminated solution obtained from Step 1, the uranium is precipitated as the "diuranate", $Na_2U_2O_7$,

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by the addition of 50% NaOH solution. Cesium is apparently not carried by the precipitate itself but by its sorbed water since the more granular precipitate, which can be produced, carries less Cs than a gelatinous material. An over-all D. F. of 100 - 1000 can be obtained through Step 2.

Step 3. The third step, which has not been worked on by Carbide and Carbon Chemicals Corporation, comprises a solvent extraction. Plutonium may probably be recovered in this step. They believe that the uranium should be decontaminated by 10^5 and that 90 - 95% recovery of the metal should be obtained.

The volume of waste from this three-step process would be about twice the original volume of metal waste solution.

They believe that, using the full centrifuge capacity of the U canyon, a production of one ton of uranium per day could be achieved. Mr Hayner stated that such production "would be a help". Dr. Hurd pointed out that they are considering the use of Nutsche-type bag filters to avoid centrifugation of the sodium diuranate; such a modification might increase considerably the rate of production since the centrifuge capacity of U canyon would be a limiting factor in the process described.

Since a solvent extraction step should probably be carried on outside the canyon, Dr. Hurd enquired regarding the possibility of new construction; Mr. Hayner replied that a process going into production six months ahead of another but requiring new construction would probably be favored.

2. Fluorination Process. In the fluorination process, starting material will be a slurry of supernate and sludge. This will be dissolved in hydrochloric acid and then hydrofluoric acid will be added. Uranium(IV) fluoride, which is very insoluble, will precipitate. Preliminary work has indicated that good decontamination factors may be obtained. Cesium and phosphate remain in solution. Fluorination of the UF_4 with elemental fluorine will be the next step and UF_6 will be volatilized. There is some indication that ruthenium follows with the uranium in the volatilization step but, since phosphate is no longer present and PF_5 therefore cannot be formed to interfere, it is hoped that some simple fractional treatment of the gaseous UF_6 may be devised to separate out the small amounts of ruthenium compound (RuF_8?) with no phosphorus interference.

Dr. H. A. Bernhardt, with associates and assistants, is concerned with this work.

3. Electrolytic Process. An ingenious electrolytic process has been proposed and some preliminary investigation of it has been carried out by Dr. McLaren and his assistants. The laboratory equipment so far used consists of a three-compartment cell with sintered-glass diaphragms, and electrodes in the outer compartments. The carbonate waste solution is fed directly into the middle compartment. Upon electroysis, the cations leave the middle compartment in one direction and the anions in the other while

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the uranium is precipitated in the middle compartment, presumably as the hydroxide. Products of the process would thus be sodium and cesium hydroxides on the one side, and phosphoric, sulfuric, and nitric acids on the other. Carbon dioxide is evolved from the acidic solution. Ruthenium goes into the anode compartment.

Since the sintered-glass diaphragm on the cation side is badly acted upon by the strongly alkaline liquors generated in the process, a study of diaphragms used in the caustic industries is being made. No difficulty is expected in finding suitable materials for the diaphragms since there is a good background of experience in this direction.

4. Ion Exchange Processes. Little work has been done on the application of ion-exchange techniques to the problem at hand. On cation exchangers, it has been found that ruthenium divides, some going on through.

A mixture of silica gel (2 g) and Fuller's earth (0.2g) has been investigated for its action on diluted synthetic Hanford metal waste solution. When the basic solution is passed through such a mixture in a column, the cesium activity is retained on the exchange material; very little uranium is held up on the column.

A final process for the recovery of uranium from Hanford waste solutions is still "a good many months away" according to Dr. Hurd. The work of Carbide and Carbon Chemicals Corporation will continue to emphasize the recovery from supernatant solutions, and particularly by use of the proposed Three Step Process. It is hoped that the sludge samples will be on hand when the new high-level laboratory is prepared to receive them.

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