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PROJECT 9536

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Explosives Department - TNX

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9. TNX Clinton Subject
10. TNX Clinton Chronologic

July 7, 1944

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DATE 3-27-62
For The Atomic Energy Commission
H. F. Carroll
Chief, Declassification Branch

JK Schure 3-28-03
JE Savely 3-13-03

CLINTON TNX TECHNICAL SECTION WEEKLY PROGRESS REPORT

JUNE 28 - JURY 5, 1944

Pile Operation

The new fan was started early in the week and has increased the total air flow by about 20%. At the same time approximately 200 partial plugs were removed from the tubes in the 100 to 150° C temperature zone described and diagramed in the report of June 7-20. These partly plugged channels were largely in the bottom and top portions of this zone. As a result of the increased flow of air in these channels the metal temperatures dropped from 10 to 30° C and thereby increased k to a point where it was necessary to insert all four shim rods to within 5' of the center of the pile and to have the two control rods at about the same relative position. This large amount of absorber acted as a poison and lowered the temperatures on that half of the pile so that the only slugs at 200° C are in a half moon shaped zone in the other half.

This situation is being corrected by an adjustment of the present poison columns and possibly by the addition of others. It is expected that this will again result in a symmetrical series of temperature zones with the shim rods out and a power output of 2200 KW. As soon as the second fan is in use the remaining partial plugs will be removed and the poisoning again adjusted to restore satisfactory temperature isotherms. The predicted power output with both fans is 2400-2600 KW.

It is the opinion here that the new fans cannot raise the pressure drop through the pile enough to endanger the roof. It is expected that the unblocking of channels will allow all the air available to pass through the pile at a safe pressure drop. As a safeguard a

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manometer and mercoid have been arranged to function between 57 to 61 inches. This situation was discussed by Mr. R. W. Smith with Mr. Webb.

Problem No. 124-X1E - Corrosion of Hanford Tubes and Slugs Under Radiation

One of the two water tubes has been operating 7 days with a charge of 40 unbonded slugs, 32 in the graphite and four in each shield wall. The second water tube contains 20 each of zinc bonded and AlSi bonded slugs 16 of each alternated in the graphite and four in the shields. This latter tube has been in operation for 4 days. The water for both tubes contains 2 ppm $K_2Cr_2O_7$, 40 parts SiO_2 as silicate and about .1 ppm iron and is being held at a pH of 7.5 and a temperature of 82-86° C. Peroxide to the extent of 2×10^{-5} N is being injected near the tube entrances. The velocity of 6 ft. per second leaves the exposure at about one fifteenth that of Hanford at 250,000 KW. No samples have been taken for bichromate decomposition as the exposure is too mild but some will be taken later when the power level is increased with the new fans.

Prior to charging the tube with the bonded slugs these were given an autoclave test to show leaks in the jackets. In this test six slugs were placed in a short section of ribbed tubing and several such pieces of tubing were inserted in a section of 8" pipe flanged off at both ends and connected to 100# (328° F 164° C) steam pressure. The autoclave was drained with a trap so that the slugs were damp but not submerged in water. The test was continued for 22 hours after which the slugs were cooled with a flow of water and removed for examination.

All of the zinc bonded slugs survived the test with no bulges but one AlSi bonded slug failed in each of the two tests with 25 slugs. The first failure caused the tube to swell and split for an inch and when the tube was cut off and the break in the slug cleaned with water, there was a cavity in the uranium about an inch in diameter and over half an inch deep. The jacket was bulged out to complete a spherical shape. This break occurred about an inch and a half from the bottom of the can and there was a crack almost all the way around the bottom at the corner* The second failure caused a tab to lift on the jacket over an area of about 1 sq. cm. This break was near the weld end and there were other smaller bulges near the edge of the can. The remaining slugs were all in good condition after the test. It appears that the autoclave method is very severe and slugs passing it should be of good quality.

*See photograph in attached Engineering Section report.

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Decomposition of Dichromate by Radiation

The work has consisted of a series of runs at a spread of pH values from 6 to 8 and for times of exposure equal to Hanford conditions. The method being used is the single exposure type where a small sample is sealed in a glass container, placed at the center of the pile for the desired time and then removed and analyzed. The method used to obtain the values given in the report of June 7-20 consists of flowing a considerable sample (5 gallons) of water through a capillary tube in the pile at such a rate as to equal Hanford exposures. Samples of exit water are taken from time to time for analyses. Although not complete the results from the two methods agree in general except that the static exposure method shows some breakdown even at pH 8. Further work must be done before the results are conclusive.

Problem No. 124-X14E - Radiation Versus Film Formation

When analyzed the solutions resulting from film removal from the two capillary tubes by oxalic acid appeared to be largely iron although they were not run for aluminum. Chromium was not present in large enough amount to give a positive result.

After cleaning, the two tubes were operated for 4 days with Hanford water to which 2 ppm $K_2Cr_2O_7$ and 40 ppm SiO_2 had been added. The pH was held at 7.5 and the iron content was the same as in the previous run, that is .1 ppm. There was an increase in pressure drop in both tubes of about the same degree (10-12%). Several samples for dichromate decomposition showed about .04 ppm an amount consistant with earlier data. After running to exhaust the supply of water the tubes were again cleaned with oxalic acid. A third run has now been started with synthetic W water again containing 2 and 40 ppm of $K_2Cr_2O_7$ and SiO_2 respectively and .1 ppm iron. The pH is being held at 8 and has varied from 7.8 to 8.2. A few sampæes for dichromate breakdown have indicated that this occurs even at pH 8. Further samples will be analyzed and the accuracy of the analytical method will be considered.

Problem No. 124-X12E - Measurement of Corrosion Currents and Potentials

In one experiment run for 36 hours the potential was measured between a slug of 2S and a 72S clad tube with proper insulation between them. This was done both with a slug near the centre of the pile and with one in the shielding. The potential with the radiated slug started at -.058^V and did not become neutral for 32 hours after which it rose to + .006^V at 36 hours when a breakdown stopped the experiment. The slug in the shield

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started at -.105^V, reached zero in 19 hours and was +.040^V at 36 hours. In neither case, therefore, was the tube protective to the jacket at first but in both cases it became so with time. This is a condition that was encountered frequently in the previous tests and the agreement between the results is sufficient to show that radiation played no part.

Testing Method for Locating a Swelled Slug in an Operating Pile

This work is still on an exploratory basis. The background in a charged tube in the SMX unit with normal water flow has been traversed for the magnitude of various frequencies and the experiment is being repeated with a slug carrying known bulges located at the centre of the tube. Pickup in this case is by a contact microphone fastened to the end cap.

If no characteristic frequencies are caused by the bulge the experiment will be repeated with the pickup in the water inside the tube to eliminate the effect of the tube walls.

In case both methods fail an attempt will be made to transmit a characteristic high frequency down the water annulus and determine if it reflects back from a known bump somewhat in the manner of radar.

SMX

The screen test has been almost completed. It was shown that the 50 mesh header screen will hold back any particles that could plug the conical tube screens even when the latter are blocked for their top halves to close the largest openings. With the finest sand used (65 - 100 mesh) the 50 mesh screen gradually plugged until with 10 grams the pressure drop was 300#. Considerable fine sand passed this screen and while it was found in the tubes there was none in the cone screens.

Further and more accurate work with water emulsions of 60 Texaco soluble has shown that the use of such emulsions during charging may permit replacement of the spline and hand crank charger with a much simpler device operated by one man. While evaluating a second type of oil an attempt will be made to design an attachment to permit hand charging by the use of an oil emulsion.

SEPARATION PLANT OPERATION

Cell Line-Up

Cells 5 and 6 were put in service with run 150. The "Clinton" pro-

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cess then in use consisted of the steps shown in column A of the table below. It was planned to start the "half Hanford" scheme with run 170 on July 6, 1944, following column B below. Adoption of the full "Hanford" process, column C below, will presumably take place about August 1.

Scheme	A	B	C
W. f. p.	No	Yes	Yes
Cell 2	extraction	extraction	extraction
Cell 3	by-product	Ce-Zr by-product	Ce-Zr by-product
Cell 5	product	product	product
Cell 6	by-product	by-product	Ce-Zr by-product
Cell 4	LaF_3 product	LaF_3 product	Bi product
Storage	--	--	8 runs held
Cell 6	--	--	by-product
Cell 5	--	--	LaF_3 by-product
Cell 4	--	--	LaF_3 product

Pre-Extraction Treatment

Formic acid was replaced by $NaNO_2$ starting with run 166 on 7-3-44. The extraction solution was made 0.1 M in $NaNO_2$ (41.5 lbs of $NaNO_2$ added with the 2400 lbs of dilution water from the dissolver) and held for ½ hour at 40° C before adding standard amounts of H_2SO_4, Bi, and H_3PO_4. The first run showed a 3.1% loss in the extraction waste solution (0.9% before skimming) while the next two each had 1.1% loss. This is far below the 10 to 20% previously found when HCOOH was omitted. Sodium nitrite will be adopted as standard unless difficulties arise.

Lower H_3PO_4 Concentration in Second By-Product Precipitation

Runs 159-163 were made with 0.02 instead of 0.1 M H_3PO_4 in the Cell 6 by-product precipitation. The objective was to lower the amount of phosphate going to room D with the product LaF_3, and so improve the oxidation of the room D two-timer while using less zirconium. It was deemed necessary, however, to return to 0.1 M H_3PO_4 when the 41 R analyses (reduced solution before LaF_3 precipitation) dropped to 12.7, 46.[illegible], 39.4, 28.0, and 68.3% of total product for runs 159-163 respectively. The Di-P analysis (HNO_3 solution of metathesized cake) of pair 158-9 showed only 52.7% which agreed with 41 R figures in suggesting a product holdup in 41 tank. It was thought that the lower H_3PO_4 concentration might have left sufficient bismuth in solution to cause bismuth oxalate which is known to carry product well to precipitate when the reducing agent was added. The Di-P analyses on pairs 160-1 and 162-3, however, both showed 120 and 110% yield, indicating pick-up of the hold-up. This theory is not water-tight, however, as at the same time lower H_3PO_4 was started in the second by-product step, the new cells

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5 and 6 were put in service. Nevertheless, after returning to 0.1 M H_3PO_4 in cell 6, the 41R sample showed 84.4% yield for run 164 and 122% for run 165. Since this value was 99.2% for run 158, the five low percents coincide exactly with the period of low H_3PO_4.

Lower HF Concentration in Cell 4

Eleven runs using 0.5 N HF for the LaF_3 product precipitation in Cell 4 showed an average loss of 1.2%. This is slightly greater than the former average of about 0.8% at 1.0 N HF, but the less corrosive conditions would appear to justify continuance of the lower amount.

Oxidation in Room D

The difficulty in oxidizing recent pairs of runs in room D, which necessitated the use of extra dichromate, zirconium, and time, has not appeared since the change to 0.02 M H_3PO_4 in Cell 6. If the trouble reappears when the 0.1 M H_3PO_4 runs reach room D, further tests will be necessary. The change being held in reserve, that is washing the LaF_3 product cake in centrifuge 42, should fill the need since this cake is not washed under present procedures.

Omission of Zirconium in Room D

Since recent isolation studies in 706-A have been handicapped by zirconium associated with the room D concentrate delivered for isolation, it has been proposed to omit the zirconyl nitrate from one or more eight-timers. It is felt that any zirconium leaking through from the two-timer (where its use now appears necessary) would probably be removed during the eight-timer steps.

RESEARCH AND DEVELOPMENT

Slug Dissolving

Problem No. 201-X248 - Solution of W Slugs

Both 15% NaOH - 13 $NaNO_3$ solution and 10% NaOH - 20% $NaNO_3$ have been compared in jacket removal tests. The former was selected for the last revision of the W flowsheet because of the possible precipitation of alumina on storing jacket solutions made with 10% NaOH. The following table summarizes the data:

Run	% NaOH/% $NaNO_3$	mols OH/mol Al	Result of treatment A	 B	 C
Ia	15/13	1.25	no ppt	no ppt	syrup

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Run	% NaOH/% NaNO$_3$	mols OH/mol Al	Result of treatment A	Result of treatment B	Result of treatment C
Ib	15/13	2.5	no ppt	no ppt	syrup
Ic	10/20	1.25	no ppt	no ppt	solid
IIa	15/13	0.83	no ppt		
IIb	15/13	1.67	no ppt		
IIc	10/20	0.83	ppt		

(Treatment A - cool and let stand four days)
(Treatment B - evaporate to 80% of volume, cool, and let stand 4 days)
(Treatment C - evaporate to 30% of volume, and cool)

The indication is that neither combination will precipitate at the OH:Al ratio of 1.25. Since the 10/20 mixture reacted less vigorously and both mixtures suspended the precipitate equally well, the 10/20 combination will be recommended for 205 Building trials and the W flowsheet.

Extraction

Problem No. 271-X18AS - $BiPO_4$ Precipitation Studies

Three types of extraction strike have been found to reduce waste losses in extractions at W product concentrations. These were compared in 3 liter scale "DS" runs. In one series of runs the reverse strike (Bi last) with 7 N Bi reagent solution and the combined strike (2/3 of Bi, all H_3PO_4, and then other 1/3 Bi) gave waste losses equivalent to the two hour H_3PO_4 (direct) strike. In another series, however, the H_3PO_4 strike gave about one-third the losses of the other methods. It appears that the reverse strike gives somewhat erratic results and the long H_3PO_4 strike is preferable.

Problem No. 203-X25S - Improvement in Decontamination

Fission product analyses of cake solutions from a standard laboratory extraction and from an extraction using fluosilicic instead of sulfuric acid showed very similar distributions of gamma activity. Since the total gamma activity was 3 or 4 times less with H_2SiF_6, it appears that a hold-back effect was exerted upon lanthanum as well as with zirconium and columbium where it was expected. Decontamination of barium was between 20 and 60 times better with H_2SiF_6 than with H_2SO_4. Relatively large amounts of H_2SiF_6 are necessary in extraction, however, since enough must be added to complex all the uranium.

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Decontamination

Problem No. 203-X253 - Improvement in Decontamination

The potential difficulty of plugging jets and lines and tanks with $BaSO_4$ from $BaSO_4$ scavenging has not been solved. Zirconium salts are not satisfactory in dissolving large quantities of $BaSO_4$. Greater attention is therefore being given the substitution of $PbSO_4$ for scavenging active barium, since this salt can be more readily dissolved.

H_2SiF_6 for semi-works trials has been received on the plant, but tests will be delayed because of the greater importance of the current semi-works program.

Fission product analyses after a Ce-Zr scavenged by-product precipitate, extraction and 1 Ce-Zr scavenged decontamination cycle indicate the chief gamma component to be lanthanum. This, and the level of activity, compares with similar observations after extraction and two Ce-Zr scavenged decontamination cycles. As previously stated, it thus appears that the same number and kind of alternate steps give quite similar decontamination regardless of which is made first. A final experiment will include a Ce-Zr by-product, normal extraction, and two decontamination cycles with Ce-Zr in by-product steps and H_2SiF_6 in product steps. Further work will then await availability of semi-works equipment.

Semi Works

The first three runs after the recent Hanford crossover experiments, 192-4, involved Bi, Ba, Ce, and Zr precipitation in the first half and Ce alone in the second half of the by-product precipitate of the first cycle. The second cycle was similar except that no $BaSO_4$ was added. The average decontamination factor through the second cycle was 10^6. The next three runs similar except that 35° C instead of 75° C was used for digestion after Ba and Bi precipitation, showed overall factors in the neighborhood of 10^4. The next three runs involving no Ba but Ce and Zr in both halves of both cycles and 40° C digestion, gave indications of low factors (10^4). It was decided, therefore, to make the following three runs, 201-3, with Ce and Zr in both parts of by-product precipitates and with 75° C digestion. This will be useful for comparison with 205 Building runs now starting with similar conditions. The steps in these cycles are briefly as follows: oxidize at 5 N HNO_3, dilute to 1.25 N HNO_3, add Bi solution, digest at 75° C, cool, add $Na_2Cr_2O_7$, add Ce-Zr solution, digest 30 minutes at 30° C, centrifuge, add more $NaBiO_3$, add Ce-Zr solution, digest 15 minutes at 30°, and recentrifuge.

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After run 203, it is planned to use plant 54P solution ($BiPO_4$ product cake after one decontamination cycle) from "half Hanford" runs as starting material for intensive study of the second decontamination cycle and the crossover. It is unfortunate that the time was too short to make two cycle semi-works runs with Ce alone in the second half and Ba omitted in the first half of the first cycle, since it is not now clear whether Ba or Ce alone was responsible for the factors of 10^6 in runs 167-170 and 192-4. Sufficient data are probably available, however, to justify later plant trials of Ce alone in the second half. This of course would not be expected to demonstrate 10^6 decontamination until the full Hanford process runs are under way in the 205 Building.

Problem No. 242-X21aS - Equipment Decontamination

Preliminary tests have been made with the 16 square foot panels painted with Tapogarth - $CaCl_2$ films. When contaminated with neutralized semi-works waste UNH solution, washing reduced the activity to background from a level of about 100 times background. With UNH solution and extraction product cake solution from 205 Building, the activity was reduced from about 300 times background to 3-5 times background.

It is believed better results are obtained if the film is applied as two coats with some time allowed for partial drying. It was found a 2 coat film could be removed by ten cycles of ½ minute spraying with a fine mist and 2.5 minute soaking. The total time was 30 minutes and the water consumption was 2 gals. per sq. ft.

Bulk Reduction

Problem No. 203-X25S - Improvement in Decontamination

Some publicity has been given to the possibility of using lanthanum oxalate for the by-product precipitate in the crossover. Laboratory tests have not shown as efficient gamma removal as when LaF_3 is used. This conclusion is substantiated by specific fission product analysis of a product cake solution obtained by precipitating $La(OH)_3$ after the by-product $La_2(C_2O_4)_3$, and dissolving the former in HNO_3. Over 40% of the gamma activity was not due to La, Ce, or Zr. Suspicion is directed toward an unknown rare earth-like cation which may be carried by LaF_3 and $La(OH)_3$ but not by $La_2(C_2O_4)_3$. The existance of such a material has been hinted at occasionally in the past, but little definite information seems available. One other fact hampers the development of a crossover cycle involving $La_2(C_2O_4)_3$ by-product and $La(OH)_3$ product pre-

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cipitates, that is the very large amount of KOH that is necessary to raise the pH of the oxalate-buffered system to a point where the product-oxalate complex is destroyed and $La(OH)_3$ is precipitated. The indications are that the amount of KOH that W would require is far above the present U. S. production and probably above the productive capacity.

Problem No. 202-X22S - Flocculation of Process Precipitates

Evidence has been obtained in the laboratory that from the point of view of ease of centrifuging the precipitate the degree of agitation is much more important during LaF_3 precipitation than during the subsequent digestion. With either pre-or co-formed LaF_3, removal by centrifuging is most complete when agitation is vigorous (comparable to that in the plant) during the strike. This indicates that the present plant pre-agitation is the most satisfactory known.

Problem No. 211-X23S - Product Isolation at W

Two semi-works tests of the straight carbonate metathesis have been conducted in the BJ equipment. In both runs a large loss (56.5% and 20.9%) was encountered in the metathesis heel. The losses in the KOH-K_2CO_3 supernatants were much less than was expected. Since the actual metathesis with K_2CO_3 has rarely given trouble in the routine isolation procedure, and since the supernatant losses mentioned above were small, a laboratory study is being started using straight tank rather than a combination of bowl and tank metathesis and somewhat larger volumes. It is anticipated that further BJ runs will be made after new conditions are worked out in the laboratory.

Problem No. 213-X67C - Hanford Isolation Studies

Three variations of the K_2CO_3 metathesis were tried on an aliquot of isolation batch 29. Procedure A was the previous "standard" method involving treatment of the LaF_3 cake (centrifuged from slurry water) with successive portions of 45% and 20% K_2CO_3 solution. Procedure B on the W scale would consist of adding solid K_2CO_3 to the 195 gallon LaF_3 slurry (from cell E of 224 Building) until the solution was 30% K_2CO_3. Procedure C was similar but a volume of 400 instead of 195 gallons was assumed for the W scale. All three involved the use of ammonium sulfide to remove iron from the K_2CO_3 solution. The following table summarizes the results;

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Procedure	Losses in Metathesis heel	Supernatant loss	% Product in final HNO_3 sol.	Fe mol
A	0.05	0.04	99.9	less than 10
B	0.02	0.2	99.8	5×10^{-4}
C	0.02	0.2	99.8	6.5×10^{-4}

These results indicate the possibility of using much larger volumes than was formerly thought safe. No peroxide precipitations were made since the results would have been meaningless in the absence of knowledge of the zirconium content of the solutions. A method for this analysis is now under study and isolation work will be considerably handicapped until a method is perfected.

Isolation

Problem No. 213-X9C - Isolation of 49 from Room D Concentrates

Batch 22, mentioned last week as started in stainless steel, was completed in glass after incomplete oxidation was found in stainless. Improper heat treating of the new vessel is suspected of contributing to the oxidation difficulty. An aliquot of batch 23 is being processed in stainless to check the results.

Problem No. 211-X23S - Hanford Product Isolation

A promising lead has been uncovered to remove iron and other impurities that cause high peroxide solubility. The suggestion consists of making a product iodate precipitation instead of the first peroxide. Since this compound has a very low solubility, it can be precipitated from somewhat larger volumes than can the peroxide. It is possible that solution of the iodate might be simpler than the method formerly used, namely reduction with SO_2 and dissolution in acid, precipitation of the hydroxide and dissolution of this in acid since new developments indicate that product iodate may metathesize readily with caustic. It is not yet known, however, if the presence of impurities in plant solutions will raise the solubility of the iodate. The metathesis procedure is also uncertain. Sufficient information should be available in another week to indicate whether this lead should be dropped or followed actively.

Problem No. 213-X67C - Hanford Isolation Studies

Data have been obtained on the filtration of product peroxide. The first experiment used three centimeter diameter Pyrex sintered glass crucibles of the "fine" and "medium" grade. As the cake was not more than 0.5 cm thick in either case it was

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not possible to obtain any evidence of change in filtration rate as the cake thickness increased. Under a vacuum equivalent to ten inches of mercury, the solution filtered at a rate of 4 ml per minute through the fine filter and 40 ml per minute through the medium filter. No solids passed through either filter since both filtrates contained only 50 mg product per liter. In a second experiment using a smaller medium filter, the final cake thickness was 1.[illegible] cm. The rate of filtration decreased markedly as the cake built up, falling off approximately in proportion to the square of cake thickness. The peroxide separated in this test occupied a volume of 1[illegible] cubic centimeters per gram of product.

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