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OAK RIDGE NATIONAL LABORATORY
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POST OFFICE BOX P
 OAK RIDGE, TENNESSEE

EXTERNAL TRANSMITTAL AUTHORIZED

ORNL
 CENTRAL FILES NUMBER

CF- 56-3-162

DATE: March 26, 1956
 SUBJECT: Chemical Development Status Report
for Week Ending March 16, 1956
 TO: F. L. Culler
 FROM: R. E. Blanco
 D. E. Ferguson

COPY NO. 33

CLASSIFICATION CANCELLED
 DATE MAR 14 1957 *fel*
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SUMMARY

Heterogeneous Power Reactor Processing

The heat of reaction on hydrochlorinating zirconium caused a rapid temperature rise within the hydrochlorinator. By introducing controlled amounts of hydrogen with a constant HCl gas flow it was possible to control the temperature of the hydrochlorinator.

Feed Materials

Recovery of thorium and mercury from Th amalgam slurries by neutral oxalate precipitation, settling, centrifugation, sludge drying and calcination resulted in thorium losses of 0.44%, and mercury losses of 0.006% of that involved in the reduction run.

The carbon decontamination factor over the reduction step in a dry ThCl_4 reduction was 16 from ThCl_4 to metal.

Vacuum drying of thorium amalgams prior to pressing and sintering resulted in improved sintered billets of thorium metal, having lowered oxide content.

Equipment Decontamination

Essentially all of the Zr-Nb and Ru and none of the Cs plated out on nickel, monel, and inconel in contact with $\text{NaF-ZrF}_4\text{-UF}_4$ fused salt containing fission products. The nickel was decontaminated by a factor of 5×10^3 (to about 0.3 mr/hr) by contacting with KHF_2 at 275°C for 6 hr.

Uranium-233-Isolation

When uranium was sorbed on Dowex-50 resin and eluted with 5 N HF, decontamination factors for Th, Zr-Nb, and Ru impurities were 160, 1.2, and 22, respectively.

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Homogeneous Reactor Blanket Processing

Titanium that was pretreated in 1.4 m UO_2SO_4 at 250°C adsorbed 20 times as much plutonium as untreated titanium. Pretreated Zircaloy-2 adsorbed 7 times as much plutonium as untreated Zircaloy-2.

Homogeneous Reactor Fuel and Blanket Studies

Thorium-uranium mixed oxide slurries at 1000 g Th per kg H_2O concentration could not be stirred in the dash-pot bomb after 67-85 hours of operation. Heating under H_2 at 275°C increased the activity of the MoO_3 catalyst in a thorium oxide slurry. Hindered settling studies are being carried out with thorium oxide slurries at $100\text{-}265^\circ\text{C}$.

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1.0 HETEROGENEOUS POWER REACTOR PROCESSING (J. E. Savolainen)

A new hydrochlorinator was constructed with a thermowell in a position to read the temperature of the reacting mass of zirconium. The observations of the temperature confirm Harrington's calculations of the large amount of heat evolved by the reaction. It was found that the temperature of the hydrochlorinator can be controlled by introducing H_2 with the HCl gas to act as a diluent.

The hydrochlorinator was filled with 30 g of 9% U-91% Zr alloy. The air was swept out with a stream of hydrogen. The temperature was then raised to $330^{\circ}C$, and the HCl gas flow was started. The temperature increased from 330 to over $400^{\circ}C$ as the HCl flow continued.

After allowing the hydrochlorinator to cool to $300^{\circ}C$, the HCl gas was again introduced at a constant rate. H_2 gas was then introduced with increasing rates until the temperature remained constant. It was possible to raise or lower the steady state temperature by decreasing or increasing the H_2 flow rate.

2.0 FEED MATERIALS (O. C. Dean)

2.1 Metallex (O. C. Dean)

2.1.1 Recovery of Thorium and Mercury from Amalgam Wash Slurries

Nine and five tenths liters of 0.5 N acid (HCl) slurry containing 230 grams of thorium and ~ 200 grams of mercury obtained from washing the product amalgam from a 4-liter reduction run at $125^{\circ}C$ were treated for recovery of the thorium and mercury. The treatment consisted of precipitation of the thorium with 5% excess acid, neutralization to a pH of 7.0 with ammonia, settling until no further sludge volume reduction was noted, centrifugation of the settled sludge, drying the centrifuged

sludge for two hours at 125°C, and finally calcination of the dried sludge at 500°C for one hour.

Settling of the untreated slurry resulted in a sludge volume of ~1% of the total slurry in 100 minutes. Settling of the oxalic acid-treated sludge resulted in a sludge volume of ~5.5% in one hour. Settling of the oxalic acid-treated and neutralized slurry resulted in a sludge volume of 57% of the original slurry in ~3 hr. Ninety-three percent of the thorium and 0.75% of the mercury remained in the untreated supernatant; 2% of the mercury remained in the oxalic acid-treated supernatant and 0.15% of the thorium and 0.22% of the mercury remained in the neutral oxalate supernatant.

Centrifugation of the neutral settled sludge for one minute and for five minutes at 1000 rpm resulted in a sludge volume reduction of 60% and 63% respectively, and 0.14% loss of thorium and ~0.7% loss of mercury to the centrifuge supernatant.

Drying of the neutral centrifuged sludge for two hours at 125°C resulted in a 63% weight loss, a negligible thorium loss and 0.01% mercury loss to the off-gas.

Calcination of the dried sludge at 500°C for one hour resulted in a 60% weight loss, a 0.15% thorium loss to the off-gas and 0.79% mercury loss to the solids. The resulting calcined oxide was 60.4% in thorium and 0.43% in Hg and contained 222 grams of thorium.

Overall losses were 0.44% of the thorium in the recovery system and 1.7% of the mercury. This amount of mercury represents ~0.006% of the mercury in the reduction run. Since only 0.75% of the mercury was lost in the settling of untreated wash slurry, some consideration will be given to a gross separation of thorium from mercury by settling of the untreated slurry.

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2.1.2 The Effect of Carbon in the ThCl_4 Feed Salt
on the Carbon Content of the Metal

A ThCl_4 feed salt which was 0.58% in residual carbon was reduced by sodium amalgam at 125°C . The amalgam product was thoroughly washed by 1 N HCl , followed by deaerated water. It was vacuum dried, stored under argon, pressed and retorted. The resulting metal contained 130 ppm of carbon by analysis and 1.82% ThO_2 . The specimen had a strong odor of acetylene as it was removed from the retort. The source of the acetylene could only have been the hydrolysis of thorium carbide, which would also result in the formation of ThO_2 . Since the usual ThO_2 content for this treatment routine was 0.6%, it was assumed that 1.2% of the ThO_2 was from hydrolysis of thorium carbide by residual water in the amalgam. The ratio of carbon to thorium in the feed salt was 9.5 mg C/gram Th, and in the metal, counting the assumed oxide equivalent, it was 0.6 mg/g Th. The decontamination factor was 16, but the residual carbon was 600 ppm or 1.5 times target specification. This indicates that the presence of residual carbon in the feed salt is undesirable for the dry reduction method.

2.1.3 Amalgam Washing Procedures

Four washing procedures were compared for effectiveness in producing sound sintered Th metal billets with low oxide content. Four amalgam samples reduced under identical conditions were washed with 1 N HCl , then deaerated distilled water in an argon-sparged container fitted with an efficient mechanical stirrer. Amalgam 1 was pressed and retorted without further treatment. Amalgam 2 was dried under vacuum for ~ 3 hours, stored overnight, then pressed. Amalgam 3 was rinsed with acetone, vacuum-dried, stored under argon, then pressed. Amalgam 4 was acetone-rinsed, stored under argon, then pressed. Results are presented in Table 1.

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Table 1

<u>Amalgam</u>	<u>Treatment</u>	<u>% ThO₂</u>	<u>Bulk Density</u>	<u>Appearance of Sinter</u>
1	H ₂ O - only	1.36	11.14	good
2	H ₂ O-vacuum dry	0.66	11.13	good
3	H ₂ O-acetone-vacuum dry	0.80	9.90	poor
4	H ₂ O - acetone	0.86	9.06	poor

The water rinse vacuum dry procedure appears to be the best of those tried. The appearance of the sintered compact was judged good if there were no deep cracks or blisters. Two bad appearing sintered compacts had a strong acetylene odor, and these (not reported in Table 1) had oxide contents of 1.20 and 1.29%. The possible explanation was that carbon in the sample reacted with thorium to produce thorium carbide, and ThC in turn reacted with residual H₂O in the amalgam to produce hydrocarbons and ThO₂. Cracking and shattering of sintered compacts could be due to the reaction of Th with H₂O to form ThO₂ and ThH₃, which later decomposed at ~ 720°C to Th + H₂.

2.1.4 The Application of a Titanium Coating to Zircaloy-2

Localized bright deposits of titanium on Zircaloy 2 ~0.5 mm in thickness which adhere strongly to the base metal have been proved by spectrographic analysis. Other bright deposits of 1 to 2 cm² have been shown to contain Zircaloy-2 constituents with small amounts of titanium. The spaces between bright deposits were coated with a dark powder, probably oxides of Zr and Ti.

Coating procedures consisted of (a) cleaning the Zircaloy specimen in a NaCl-KCl-ZnCl₂ bath at 450°C dipping in molten zinc, washing in mercury, coating directly with titanium quasi-amalgam, then heating in vacuum or argon atmosphere to 950-1050°C to remove Hg and Zn residues; (b) cleaning in a bath of NaCl-KCl-SnCl₂, dipping in molten tin, washing off the tin with Hg, coating with titanium amalgam

then retorting as above. Some of the specimens thus cleaned were coated with washed titanium amalgam, and some with unwashed TiHg_x . Those coated with unwashed TiHg_x gave completely unsatisfactory results. The two treatment procedures outlined above were about equally effective in producing coatings. The atmosphere of the retort was an important factor in producing oxide-free coatings.

3.0 EQUIPMENT DECONTAMINATION (R. E. Leuze)

3.1 Volatility Equipment Decontamination (R. D. Baybarz)

Essentially all of the Zr-Nb and Ru activity plated out on nickel, monel, and inconel from $\text{NaF-ZrF}_4\text{-UF}_4$ fused salt containing fission products. Essentially none of the Cs plated on the metals.

Nickel, monel, and inconel coupons were suspended in an equimolar mixture of NaF and ZrF_4 during dissolution of irradiated uranium metal. Only a trace of Ru and no Zr-Nb was found in the fused salt after the uranium dissolution.

A nickel coupon with a small amount of NaF-ZrF_4 salt clinging to it read 400 mr/hr at 1/2 in. The Cs γ activity on this sample was 1.2 times the Zr-Nb activity, and the Ru γ was 3.4 times the Zr-Nb γ . This sample was then placed in KHF_2 at 275°C for five minutes to dissolve the NaF-ZrF_4 . After this treatment the coupon read 20 mr/hr at 1/2 in. The Cs γ activity was only 0.1 times the Zr-Nb γ activity, and the Ru γ was 3 times the Zr-Nb γ . From these results it appears that both Ru and Zr-Nb were adsorbed on the metal and the Cs was essentially all in the salt.

In two decontamination experiments, the activity on two nickel samples was reduced from 900 and 700 mr/hr to 0.3 and 0.15 mr/hr, respectively, by contacting them with molten KHF_2 at 275°C for 6 hr. These correspond to decontamination factors of 5×10^3 and 3×10^3 .

There was no replating of activity on the metal samples even though the KHF_2 was reading 30 mr/hr at contact.

4.0 URANIUM-233 ISOLATION (R. E. Leuze, W. E. Tomlin)

When uranium containing thorium and fission products was loaded on Dowex-50 cation exchange resin and eluted with 5 N HF, decontamination factors for Th, Zr-Nb, and Ru were 160, 1.2, and 22, respectively.

One-half liter of uranyl nitrate solution containing 20 g U/l, 0.5 g Th/l, and tracer amounts of Zr-Nb and Ru was passed through a column containing 40 ml of Dowex-50 resin. Elution with 40 ml of 5 N HF removed 96.8% of the uranium.

5.0 HOMOGENEOUS REACTOR BLANKET PROCESSING (R. E. Leuze)

5.1 Plutonium Adsorption on Metals (J. M. Chilton)

Titanium that was pretreated in 1.4 m UO_2SO_4 at 250°C under air for 16 hr adsorbed 20 times as much plutonium as untreated samples. Pretreated Zircaloy-2 adsorbed 7 times as much plutonium as untreated samples.

Three series of adsorption tests were made. In all tests metal coupons were suspended in 1.4 m UO_2SO_4 containing 1.3 mg Pu/kg H_2O . The solutions were heated to 250°C in a Pyrex glass lined autoclave under 190 psi H_2 and 95 psi O_2 .

In one series of tests both untreated coupons and coupons preconditioned for 16 hr at 250°C in 1.4 m UO_2SO_4 were used. Plutonium adsorption after 80 and 96 hr, respectively, was 2.36 and 2.40 $\mu\text{g}/\text{cm}^2$ on the pretreated titanium, 0.10 and 0.11 $\mu\text{g}/\text{cm}^2$ on

the untreated titanium, 1.78 and 1.86 μ g/cm² on the pretreated Zircaloy-2, and 0.23 and 0.28 μ g/cm² on the untreated Zircaloy-2.

In another series, only untreated titanium and Zircaloy-2 coupons were used. Plutonium adsorption after 16 and 32 hr, respectively, was 0.05 and 0.11 μ g/cm² on titanium and 0.08 and 0.13 on Zircaloy-2.

In the third series, untreated coupons of titanium and type 347 stainless steel were used. Plutonium adsorption after 16, 32, and 48 hr, respectively, was 0.03, 0.03, and 0.03 on titanium and 0.05, 0.11, and 0.26 on stainless steel.

5.2 Stability of Glass to UO₂SO₄ (J. M. Chilton)

When 1.4 m UO₂SO₄ was heated at 250°C in autoclaves lined with Pyrex, a small amount of silica precipitate was noted after the first exposure but not after subsequent runs.

6.0 HOMOGENEOUS REACTOR FUEL AND BLANKET STUDIES (J. P. McBride)

6.1 Thorium Oxide Slurry Irradiation Studies (A. R. Jones, N. A. Krohn)

LITR experiment #19, containing 1000 g Th per kg H₂O of a thorium oxide=0.5% enriched uranium oxide, was inserted in hole C-44 of the reactor on March 14, 1956. The slurry was stirred without difficulty at 300°C for 85 hours, 69 hours under irradiation. The stirrer then stopped operating and while it could occasionally be restarted it could not be kept running. In an out-of-pile control experiment the duplicate slurry was stirred easily for 67 hours after which stirring became erratic. The difficulty with stirring in both cases probably resulted from a degradation of the oxide particles on prolonged stirring and consequent thickening of the slurry.

The mixed oxide was prepared from the coprecipitated tetravalent oxalates by a multistage calcination ending at 900°C .

6.2 Slurry Viscosity Measurements in the Dash-Pot Irradiation Bomb (N. A. Krohn)

Apparent slurry viscosities were measured for several more materials using a dash-pot irradiation bomb controlled by a Thyatron timer. Average viscosities over the temperature range $50\text{--}250^{\circ}\text{C}$ for 650°C fired D-16 were 3.9, 4.8, 7.1, 12.6, and 27.4 centistokes at concentrations of 250, 500, 750, 1000 and 1250 g of Th per kg H_2O . The average viscosities for slurries of a mixed oxide, prepared by autoclaving 650°C D-16 with 0.5% natural U as $\text{UO}_3 \cdot \text{H}_2\text{O}$ and refiring at 900°C , were 3.5, 3.8, 5.1, 6.8 and 11.0 centistokes under the same conditions of temperature and concentration. A similar preparation using enriched U showed higher viscosities of 5.3, 6.8 and 18.2 centistokes at concentrations of 250, 500 and 1000 g Th per kg H_2O . This material at a concentration of 1000 g Th per kg H_2O became pasty after prolonged stirring at 300°C giving viscosity readings as high as 32 centistokes before the plunger became inoperative.

6.3 Gas Recombination Studies (L. E. Morse)

A freshly prepared slurry containing 1000 g Th per kg H_2O of a 900°C fired oxide, 0.5% by wt. UO_3 (based on ThO_2), and 0.1 molal MoO_3 gave a hydrogen-oxygen recombination rate of .7 moles of hydrogen per hour per liter of slurry at 275°C and a hydrogen partial pressure of 500 psi. Prior to running the combination experiment the slurry was preheated at 280°C under an O_2 atmosphere (300 psi O_2 at room temperature).

Heating the above slurry under hydrogen for 2.2 hours at 275°C (1000 psi H_2 at room temperature) increased the catalytic activity. The hydrogen-oxygen combination rate with the reduced slurry was 16 moles of hydrogen per hour per liter at 115°C and $P_{\text{H}_2} = 500$ psi.

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The reduced slurry also showed strong catalytic activity at room temperature which decreased with repeated experiments.

Reheating the slurry for 2 hours at 280°C under O_2 (500 psi at room temperature) did not reduce its catalytic activity. The reaction rate with the oxidized slurry was 31 moles of hydrogen per hour per liter of slurry at 206°C ($P_{\text{H}_2} = 500$ psi).

The MoO_3 was prepared by heating ammonium paramolybdate at 480°C for 18 hours. The ThO_2 , $\text{UO}_3 \cdot \text{H}_2\text{O}$, and MoO_3 mixture was tumbled dry for 1 hour before dispersing it as an aqueous slurry.

6.4 Hindered Settling Studies at Elevated Temperatures (V. D. Allred, J. P. McBride)

An apparatus has been developed which permits the study of the settling characteristics of thorium oxide suspensions at elevated temperatures in stainless steel equipment by continuously photographing the settling slurries by x-ray techniques. The initial data obtained with the apparatus has exceeded expectations. The water-vapor and slurry-water interfaces are clearly indicated on the x-ray film for slurries as dilute as 250 g Th per kg H_2O , x-ray energies of 180-200 kv, and film transport speeds of 2 in. per sec or exposure times of 0.15 sec.

The hindered settling characteristics of several pumped slurries are being determined over the temperature range of 100 to 265°C . At 500 g Th per kg H_2O concentration all the pumped slurries so far tested (D-16-900-24, T0-10-900-24, P0-10-900-24) appear to be in or near compaction.

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