UNCLASSIFIED

HW--34868-C6

DE92 007560

1. AL Bement	32. GA Last
2. TK Bierlein	33- 35. HC Mayer
3. R. Bloomstrand	36. WW McIntosh
4. D. Bolender	37. DW McKee
5. SH Bush	38. DW McLenegan
6. PA Carlson	39. JE Minor
7. VR Cooper	40. LP Morgan
8. WV Cummings	41. WS Nechodom
9. PW Dickson	42. WJ Ozeroff
10. TW Evans	43. OH Pilkey
11. JM Fouts	44. H Radow
12. CE Frantz	45. OW Rathbun
13. MC Fraser	46. RL Reynolds
14. MD Freshley	47. JW Riches
15. JW Goffard	48. WE Roake
16. CN Groot	49. J. Roslund
17. GB Hansen	50. W. Royce
18. AW Hervin	51. MJ Sanderson
19. JD Hoffman	52. ML Smith
20. DL Hovorka	53. WR Smith
21. HH Hubble	54. RM Smithers
22. RE Hueschen	55. GL Swezea
23. FE Jochen	56. RD Switters
24. BF Judson	57. RH Todd
25. AJ Karnie	58. RE Vandercook
26. WT Kattner	59. WP Wallace
DC Kaulitz	60. DK Warner
RS Kemper	61. RG Wheeler
LF Kendall	62. OJ Wick
WK Kratzer	63. DL Zimmerman
LW Lang	64. 300 File
	65. Yellow Copy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Classification cancelled (or changed to Confidential)

by authority of the from Doc 8-8-57

by C.P. Burgess TIE, date 9-12-57

This document consists of 17 pages.

NUCLEAR METALLURGY LECTURES

UNCLASSIFIED

Chapter 6
REDUCTION OF URANIUM

May 26, 1955

864 - 001

UNCLASSIFIED

- 2 -

HW-34868 C6

FIGURE 1
GENERAL FLOW OF URANIUM IN HAPO PU PRODUCTION STREAM

NUCLEAR METALLURGY LECTURES

Chapter 6

Reduction of Uranium

A. ORES

1. Types

- a. Carnotite - Approx
- 47% U_3O_8
 - 21% U_2O_5
 - 11% SO_4
 - 8% Na
 - 4% Cl

b. Pitchblende

	Typical Compositions		
	High grade (70 % U_3O_8)	Medium (25% U_3O_8)	Low (8-10% U_3O_8)
U_3O_8	69%		7.9 %
PbO	6		0.9
SiO_2	10		50.
Fe_2O_3	0.3		.04
Al_2O_3	1.6		8.
MoO_3	0.8		0.2
CaO	2.5		0.7
NiO	0.8		
MgO			12.

Ra, Pb, and Mo are present
Va is absent

Pb roughly proportional to U_3O_8 ; MoO_3 variable.

c. Torbenite

17.7%	U_3O_8	
51.1	SiO_2	
1.9	Fe_2O_3	50 % Quartz
6.5	Al_2O_3	30 % Green crystals
5.2	MgO	Copper uranium phosphate
4.6	P_2O_5	(characteristic of torbenite)
2.8	CuO	10% Black mineral (mixture
1.2	NiO	of oxides)
0.3	MoO_3	
0.2	CoO	
0.4	U_2O_5	

- d. Good discussion, Katz & Rabinowitch, see bibliography No. 12.

0315587030

- 4 -

HW-34868 C6

2. Sources

a. Domestic - Early in project history were not processed principally for U. U was a by-product of Vanadium from Carnotite or residues in stock piles from Va operations.

1. Pitchblende - with torbenite, Autenite, Uranite (New strike at Lake Athabasca, Great Bear Lake)
(20-30 kinds) Principal sources in early MED days. MCW Plant 4 operated on Canadian black oxides as did duPont & Linde Air Products.

2. Carnotite - Colorado - Va was a headache
- Now about 10 concentrating mills - privately owned.
- Use their own processes (not known to AEC)
- Break even point 0.2% U - a/c handling costs
- Domestic production now equals Belgian Congo.

3. Phosphate Rock - Florida leached zone materials
- In .01% U range.

b. Foreign

1. Pitchblende et al - Belgian Congo - Radium initial objective
- outstanding source - Upper Katanga
- MCW Plant No. 6 Built in 1945 to process this ore.

2. Rand - S.A. - Tailings from cyanide gold process
- U low, but tailings above ground
- Concentration by ion exchange process developed AEC @ Watertown Arsenal - Turned over to South Africans. AEC partially financed building. Now a major producer - expected to outstrip every other source. Concentrate will probably go mostly to NLO.

3. Australia - North - Rum Jungle - Dandite, an iron titanate matrix, concentrated by ion exchange
South - Radium hill
MCW will pilot plant extracts in U.S.
High Ti and Cu ores - problems quite different - Expected to become an important source.

4. Portugal - Minor source

5. Czechoslovakia - Important to USSR

3. Abundance of Uranium

a. More abundant than Cd, Bi, Hg, Ag

b. 0.0004% of earth's crust.

031712881030

004

- c. Highest in igneous rocks; $\frac{1}{2}$ as much in sedimentary rocks
- d. Principal ores are
1. Pitchblende - accompanied by secondary ores, by leaching, :
Torbernite
Autenite
- a hydrous oxide of Pb and U
 2. Carnotite - hydrous K, U, Va oxides
- e. Minor ores
1. Zeunerite - Cu-U arsenate (hydrous)
 2. Uranospinite - do
 3. Uranocircite - B - U phosphates
- f. U found combined as columbates, tantalates, titanates, phosphates, sulphates, and arsenates. Generally these are not commercially important.

B. ORE CONCENTRATION

1. Sulfuric acid process not suitable for high calcium ores. See Ref. 3 for typical flow sheet.
2. Carbonate process. ~ 10% Na_2CO_3 solution to leach high calcium ores. See Ref. 3 for typical flow sheet.
3. Ion exchange column. (See Fig. 2 for typical process.) Important in working tailings, picked over ore residues in Belgian Congo. Strong base anionic resins, made by Rohm & Haas, adsorb uranyl sulfate. Pellets produced compare with hand picked pitchblende. Va picked pitchblende runs 35-40% U.
4. Resin in pulp process, Fig. 3, used to concentrate low value Colo. Plateau ores.
5. General Process for Concentrating Florida Leached Zone Material in Fig. 4.

Ore Concentrating Plants

<u>Company</u>	<u>Location</u>	<u>Process</u>
U. S. Vanadium	Rifle, Colo	Acid
	Uravan, Colo	"
N. Corp. Am.	Naturita, Colo.	"
	Durango, Colo.	"
Climax Molybdenum	Grand Junction, Colo.	"
Vitro Chem	Salt Lake, Utah	"
AEC (Gallagher)	Monticello, U.	Carbonate
Anaconda	Shiprock, N. M.	Ion exchange, acid
Kerr-McGee	--	" " "

0311597030

- 6 -

HW-34868 c6

FIGURE 2
ION EXCHANGE COLUMNS

031712281030

000

0315507030

- 7 -

HW-34868 C6

FIGURE 3
RESIN IN PULP PROCESS

FIGURE 4
FLORIDA LEACHED ZONE MATERIAL
GENERAL PROCESS

03172281030

007

C. EXTRACTION PROCESS

1. Ether

- a. Initial work was done by J. I. Hoffman, NBS.
Developed to a high state of efficiency at the MCW.
- b. Procedure Average efficiency 99.7%

1st
step

Ore Solution Containing:

Continuous
ether extraction

Washing of extract

Strip of U from
solvent in columns Reextraction of
UNH with ether
$$\left\{ \begin{array}{l} 3900 \text{ ppm MoO}_3 \\ 1900 \text{ ppm P}_2\text{O}_5 \\ 360 \text{ ppm SiO}_2 \\ 5000 \text{ ppm Fe} \end{array} \right\}$$

$\text{Ca}(\text{NO}_3)_2$ or NaNO_3 used as a salting out
agent to increase partition coefficient

- c. Detailed MCW schematic in Fig. 5.

2. TBP - Ether Comparison

- a. Can use a stronger acid concentration than ether.
- b. Distribution coefficient is higher, particularly at the bottom of the column.
- c. Ether extraction provides 99.7% Recovery
TBP extraction provides 94.95% Recovery
- d. TBP approaches saturation sharply; has a lower U carrying capacity than ether (factor of 3). Consequently requires a larger capital investment for plant than ether.
- e. TBP approaches ether in purity of extract in one cycle, exceeds one cycle of ether in purity in two cycles.
1. Ether is less favorable for boron removal and more favorable than TBP for removal of thorium.
- f. The "scrub" (sprinkling of a small amount of water through OK extract to remove Fe and Boron) make the FMPC(TBP) process, a one cycle deal.

FIGURE 5
FLWSHEET - ETHER EXTRACTION AS CURRENTLY PRACTICED AT MCW

g. "Obex" - Weldon Spring, one stage TBP, second stage ether.
This has just recently been confirmed for design.

h. FMPC Flow:

D. ORANGE SALT IS PRODUCED BY DENITRATION
IN STAINLESS STEEL POTS AT MCW,NLO

Pots ca 3' dia by 2½' deep. Have tried both cast and welded pots, but have continuous corrosion problems, consequently pick up constituents of stainless at this point to a small degree in UO_3 . Part of problem due to hot spots in gas firing at MCW and NLO. Not an entirely satisfactory process, but nothing better is in production use; however, Sep. Tech's rotary kiln seems to have promise.

E. GREEN SALT

Slide #7, HW-35577-SL shows schematic of process, conversion of UO_3 to UF_4

1. Production rate @ MCW 300-350 # UF_4 /hr.

2. Hydraulically driven ribbon screws

3. 150 % excess anhydrous HF

4. 55 % excess cracked ammonia

5. Zone temperatures $UO_3 + H_2 \rightarrow UO_2 + H_2O$ 1200 F
 $UO_2 + HF \rightarrow$ 650 increasing gradually to 1100 F

6. Flights on Screws (3)

Ilium "R" - Expensive, difficult to obtain, co. now thought to be broke.

Inconel - 79% Ni, 13.5% Cr, 6.7% Fe, 0.7% Mn, 0.2% Cu

Hastelloy C - 57% Ni, 14.0 % Cr. 6.0 % Fe 5.0 W 18% Mo
(Not readily worked - possibly "B")

7. UO_3 converted to UO_2 in first tube

UO_2 converted 75-80% UF_4 @ 650-850 in 2nd reactor tube

UO_3 converted 90-93% UF_4 @ 850-950 3rd Reactor tube

UO_2 converted ~ 97% UF_4 @ 1000-1100 4th " "

0313597030

- 11 -

HW-34868 C6

F. BOMB REDUCTION - THERMAL REDUCTION DEVELOPED BY F. H. SPEDDING AND ASSOCIATES
AT IOWA STATE COLLEGE

1. Conventional Bombs Made with Pipe with Flange for Bolting on Lid

Reduction Reactions:

Liner - electrically fused dolomite (NLO)
MgF₂ (slag liner) (MCW)

Charge 100 Mesh UF₄

Granular Mg - usually 4-10% stoichometric excess

REDUCTION (MCW)

	<u>8-Inch</u>	<u>12-inch</u>
Green Salt (UF ₄) Charge	150#	400#*
Mg + 2-4% Excess	24#	65#
Weight of Derby Produced	105-110#	290-300#
Average Yield	96.5%	97%
Diameter	7½-8"	11½-12"

*UF₆ → UF₄ Type Green Salt (480 lbs.)

PROCESSING DETAILS (MCW)

	Time (min.)	
	<u>8-inch</u>	<u>12-inch</u>
Pot Lining	20	22
Pot Charging	15	20
Pot Capping	10	20
Reduction (Firing Time)	130	164
Air Cooling	30	90
Water Cooling	120	150
Derby Breakout, Cleaning & Pot Cleaning	<u>10</u>	<u>15</u>
Total Cycle	335	481
Furnace Temperature	1225-50 F	1225-50 F
Metal Production Rate	.33 lbs./min	.61 lbs./min.

0317229.0301

Placed in soaking pit or furnace at ~1200 F

Fires at temps. between 950-1200 F. Max. Temperature attained 3500 F

2. Objective - to obtain high purity material with a minimum of exogeneous inclusions.
3. Green salt to ingot yield ca 71.2%. Dingots expected to be equivalent or better.
4. Cleanliness improves with derbys size due to better segregation of uranium
5. Chemical Composition

	8-Inch		12-Inch	
	T	B	T	B
Carbon	20	15	32	37
Nitrogen	25	35	32	37
Magnesium	31	37	25	20

6. Derby Pickling

AVERAGE PICKLING RATES OF 300 POUND DERBIES IN 50% HNO₃ at 150F

Total Pickling Time - hours	Average Weight Loss, % of Original Weight			
	Uranium	1.5% Silicon- Uranium	0.5% Titanium- Uranium	1.5% Silicon- 0.5% Titanium-Uranium
1/3	2.5	9.1		8.7
1/2	3.8	12.2	3.4	10.8
1	6.0	12.1	4.8	19.0
2	8.0		6.4	

Effect on chem. analysis and density tabulated on next page.

COMPARISON OF PICKLED AND UNPICKLED DERBY HEATS
(Seven Inch Diameter)

Sample Level, Inches from Ingot Bottom	Carbon ppm		Density g/cc		Magnesium ppm		Nitrogen ppm	
	Heat 637P	Heat 646u	Heat 637	Heat 646	Heat 637	Heat 646	Heat 637	Heat 646
44	--	300	--	19.01	--	1.9	--	28
43	--	320	--	18.98	--	2.0	--	37
42	1140	300	17.98	18.98	500	3.7	1000	29
41	330	320	18.99	18.98	4.8	2.4	46	28
40	320	340	18.98	18.98	4.8	1.9	37	31
39	310	310	18.99	18.99	4.7	2.1	48	30
38	330	320	18.98	18.98	2.8	1.9	45	35
37	330	300	18.98	18.95	4.9	2.1	41	46
36	300	340	18.97	18.97	4.2	3.2	46	42
35	320	300	18.96	18.96	20	7.6	71	33
30	300	340	18.98	18.97	150	5.8	68	32
25	300	320	18.97	18.99	30	15	70	20
20	290	300	18.97	18.97	15	7.8	61	35
15	390	320	18.98	18.96	8.7	7.2	56	21
10	280	340	18.96	18.99	5.8	2.2	56	29
5	290	290	18.96	18.99	2.9	2.5	57	29
Bottom	290	280	18.95	18.98	4.0	4.0	63	27

G. MELTING AND CASTING

1. Vacuum induction melting; graphite crucible and mcl.d;
MG set; 3000 cps
2. Poured by breaking a graphite plug. Average charge is about 1000 lbs.
cast into ~ 7" dia. mold.
3. Pressure usually 200 microns or less.
4. Melting Cycle data

	<u>5"-600# Charge</u>		<u>7"-1200# Charge</u>	
Melting Cycle	85 KW	43 Min.	100 KW	5 Min.
	25 KW	15 Min.	175 KW	40 Min.
	60 KW	<u>28 Min.</u>	100 KW	<u>30-35 Min.</u>
Total		86 Min.		75-80 Min.
Pour Temperature	2500 F		2550 F	
Cooling Cycle	90 Min.		120 Min.	
Ingot Stripping	10 Min.		10 Min.	
Furnace Breakdown	<u>20 Min.</u>		<u>20 Min.</u>	
	206 Min.		230 Min.	

5. Pouring temp a compromise between
- a. Low C & N with low pouring temp
Poor surface quality with low pouring temp } 2475 F
 - b. Reverses the above at 2650 F i. e.,
Less piping at the higher temperature, especially with hot topped
molds, directional cooling.
 - c. 7" Molds, hot topped permit lower pouring temperatures, 2400 F
6. Crucible wash often used } Mixture MgO and MgSO₄ or MgCl₂
Mold wash often used } in water.
7. Arc melting used for alloys for homogenization.
8. British have done a lot of melting under flux but recently have gone
to use of a vacuum.
9. Chemical Composition Comparison between 500# and 1000# ingots!

CHEMICAL COMPOSITION (MCW)

	<u>5" Ingot</u>	<u>7" Ingot</u>
Carbon	350-450 ppm	200-300 ppm
Nitrogen (Bottom)	45-55 ppm	35-45 ppm*
Density (Top)	18.90-18.92	18.96-18.98
Density (Bottom)	18.95	18.98-19.01
Iron	75-85 ppm	70-80 ppm
Nickel	30-40 ppm	25-35 ppm
Silica	20 ppm	20 ppm

* Top and Bottom Analyses

10. Comparison of yields between 5" and 7" ingots

INGOT CHARACTERISTICS (MCW)

	<u>600# Charge</u>	<u>1200# Charge</u>
Crude Ingot Weight	570-580#	1165-1180#
Cropped Ingot Weight	520-530#	1095-1110#
Length, Crude	41"-45"	46"-48"
Length, Cropped	36"-40"	43"-45"
Yield, Crude	95-96%	97%
Yield, Cropped	87-88%	91%

0315087030

- 15 -

HW-34868 C6

H. DINGOTS

1. Processing losses - high in scalping 1400-400 = 1000#
But about 50% yield g.s. to good slugs - compares with present production.
2. Bomb design
See Ref. 10 MCW quarterly reports for photos and for bases for designs
3. Factors Affecting Yield - See Ref, 13 a for slides or MCW quarterly reports
4. Density: ca 19.00, Slide 5
5. Analysis compares favorably with best laboratory prepared uranium.
6. MCW has within last month found large charges can be fired with 7 lb. excess over stoichiometric requirements for Mg, regardless of dingot size.

W. T. Kattner

BIBLIOGRAPHY

1. Vance, J. E., and Warner, J. C. Uranium Technology, General Survey, NNES, VII, 2A

An overall view of the technology of uranium production as practiced prior to 1946.

2. Warner, J. C. et al., Metallurgy of Uranium and Its Alloys, NNES, IV, 12A.

An overall view of the development work completed on the Manhattan Project.

3. RH-3 Reactor Handbook - Vol. 3

A general description suitable for Handbook information. Somewhat dated in much of the data.

4. Extraction of U and Th from Monazite Sands

ORNL-1859, dated 2-1-55

Not discussed in lecture; development and pilot plant work to date.

5. J. Van Impe, Uranium and Fabrication, Chemical Engineering Progress, May 1954, p. 230-4

Belgian processes with some historical review.

Pictures of equipment used for ~60# charges with open bomb.

6. Solvent Extraction of U and V from Colo. Plateau Ores

DOW-125 dated 1-1-55

DOW-127 dated 3-1-55

7. Recovery of U from Florida Leached Zone Material

DOW-125 dated 1-1-55

DOW-127 dated 3-1-55

RMO-2733 dated 2-25-55

8. Resin in Pulp Process Development

ACCO-65 dated 8-5-54

WIN-5 dated 1-11-55

WIN-3 dated 2-21-55

RMO-2616 dated 3-23-55

9. Solution of sliming problem by Non-Aqueous Extractive Methods.
for Colo. Plateau Ores

BMI-279 dated 2-9-55

BMI-280 dated 2-22-55

0315587030

UNCLASSIFIED

HW-34868 C6

BIBLIOGRAPHY (Continued)

10. Quarterly Technical Reports from NLO and MCW

Give status of development programs and production problems at two sites from extraction of concentrates through casting. Additional work on fabrication. Typical recent documents:

<u>NLO</u>	<u>MCW</u>
FMPC 475	MCW - 1372
FMPC 437	MCW - 1371
FMPC 405	MCW - 1370
FMPC 404	MCW - 1369
FMPC 365	MCW - 1367
	MCW - 1373

11. Lemmon, A. W. et al, The Thermodynamics of the Reduction of Uranium Compounds to Uranium Metal, BMI-550, July 21, 1952

12. Katz, J. J. and Rabinowitch, E., Chemistry of Uranium, Part I, McGraw Hill, 1951

Declassified Discussions:

Chap. 3 Uranium in Nature - A good description of ores and minerals.
Chap. 4 Extraction of Uranium from Ores and Preparation of Uranium Metal.

13. Slides used are documented:

- a. HW-35577-SL
- b. HW-35964-SL

UNCLASSIFIED

END

**DATE
FILMED
3 / 16 / 92**