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PRODUCTION OF URANIUM TETRAFLUORIDE AND URANIUM METAL

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ABSTRACT

The main sources of feed materials are given for the production of uranium tetrafluoride and uranium metal at the National Lead Company of Ohio. The historical background of uranium tetrafluoride and uranium metal production facilities is presented together with the primary manufacturing techniques currently in use.

INTRODUCTION

It has been some years since the production technology of uranium tetrafluoride and uranium metal was updated in the literature. Although the book, Uranium Production Technology,¹ (published in 1959) is generally regarded as the basic source of information on feed materials and uranium metal technology, we believe it is now timely to report on current practices at the National Lead Company of Ohio.

Much early work on the technology of uranium production was performed by Spedding, Wilhelm,² and co-workers at Ames Laboratory, Iowa State University. Wilhelm's report in the Journal of Chemical Education³ on these war-time activities is both informative and entertaining. Later, when the production of uranium was shifted to industry, a number of companies shared in the development of production technology. Among the more important contributors were Mallinckrodt Chemical Works, St. Louis, Mo., Union Carbide Corporation, Oak Ridge, Tenn. and Paducah, Ky., E. I. duPont, Chambers

Works, Del., Electro Metallurgical Company, Niagara Falls, N. Y., Harshaw Chemical Works, Cleveland, Ohio, and the National Lead Company of Ohio.

At present, two large-scale production facilities remain in the AEC complex for uranium tetrafluoride and uranium metal production: the Feed Materials Production Center (FMPC) at Cincinnati (Fernald), Ohio, operated by National Lead Company of Ohio, and the gaseous diffusion plant at Paducah, Kentucky, operated by Union Carbide Corporation. The primary emphasis at the FMPC is on the production of uranium metal fuel core products, while the Paducah facility primarily converts UF_4 to UF_6 for gaseous diffusion (isotope separation).

URANIUM TETRAFLUORIDE PRODUCTION

Uranium tetrafluoride, or "green salt," is the key intermediate compound^d in the production of uranium metal. Uranium tetrafluoride is also an intermediate in the production of UF_6 , the compound employed in the gaseous diffusion operations, as mentioned above, for separating ^{235}U from ^{238}U . This activity is becoming increasingly significant in supplying fuel for the commercial nuclear power industry.

The starting material for the production of UF_4 is UO_3 , which is known as "orange oxide". This oxide is the product of the thermal denitration of purified and concentrated uranyl nitrate. The physical and chemical properties of the orange oxide determine, to

a large extent, the processing characteristics of the material as it goes through the subsequent production operations. The main chemical reactions involved are

and

Figure 1 shows the production flow diagram.

The orange oxide used to make UF_4 comes from several sources and contains various percentages of ^{235}U ranging from less than 0.2% ^{235}U through the natural 0.7% to as high as 2% ^{235}U . We have not consumed any ore concentrates from the AEC inventory for over one year. The current primary sources of orange oxide are as follows:

1. From the FMPC Refinery and orange oxide facility (indirect gas-fired stirred-pot denitration). The Refinery feed consists of residues from various uranium metal operations, residues and surplus materials from various off-site uranium programs, uranyl nitrate from Nuclear Fuel Services, West Valley, N. Y., as separated from irradiated AEC and commercial nuclear reactor fuels.
2. Savannah River, South Carolina (E. I. duPont), from irradiated fuel reprocessing (electrically heated stirred-pot denitration).
3. Hanford, Washington (Atlantic Richfield Hanford Company), from irradiated fuel reprocessing (electrically heated stirred-trough denitration).

As will be discussed later, each of these orange oxide feed materials has its own peculiarities which require special attention.

Table I lists the specifications for UO_3 from natural uranium. In the specifications, the metallic impurities are essentially set by the tolerance in the uranium metal produced from the UO_3 . Sodium is an exception, as this impurity has a detrimental effect⁴ on the reaction of the HF and UO_2 . Sodium forms relatively low-melting mixed salts with the UF_4 which restrict the reaction of HF and the unconverted UO_2 . Quantities above 100 ppm can lead to more serious problems in the reactor tubes by forming plastic masses which cause high feed screw torques or plugging.

Orange oxide from our Refinery and, generally, that from Savannah River is processed to UF_4 in a straightforward manner. A hopper of orange oxide containing about 5 tons is placed on a weight-scale feed system and is fed through a seal hopper into the first stage of a two-stage fluidized bed reactor (operated at $1100^\circ \pm 50^\circ\text{F}$) with dissociated ammonia ($\text{N}_2 + 3\text{H}_2$) as the fluidizing and reducing gas. The UO_3 is reduced to UO_2 or "brown oxide"; the brown oxide from the fluid bed unit is conveyed through a ribbon-screw horizontal-tube reduction reactor (that had originally been used for the UO_3 -to- UO_2 reduction) and discharged into another seal hopper which feeds a series of three hydrofluorination ribbon-screw reactors. The UO_2 is gradually converted to UF_4 as it is mixed and moved forward and downward through this series of reactor tubes; anhydrous HF is metered into the bottom reactor tube (solids discharge end) and flows countercurrent to the solids flow.

The Hanford orange oxide requires a more vigorous treatment to produce top-quality UF_4 . This oxide is reduced to UO_2 in a fluid bed reactor, is reoxidized to U_3O_8 ("black oxide"), and then is fed as black oxide to the standard bank of reactors for reduction to UO_2 and hydrofluorination to UF_4 .⁵

Several significant improvements during the last 15 years have led to lowering overall production costs. The first of these was the improved reaction performance realized when about 1500 ppm (uranium basis) sulfate was added as sulfuric acid to the denitration pot charge.⁶ Another involved the successful development of the fluidized bed reduction reactor⁷ (mentioned above) in which the UO_3 is reduced to UO_2 . It was realized earlier that the exothermic reduction reaction had to be done carefully so that thermal damage was not done to the UO_2 (or intermediate U_3O_8) since this would lead to problems in getting high conversion levels in the UF_4 step. The fluid bed reactor gave the desirable, nearly uniform, temperature control for practically each oxide particle during conversion and yielded a UO_2 product which could be hydrofluorinated at several times the feed rate previously employed. These improvements permitted the simple condensation of the hydrofluorination off-gas as about 30% aqueous HF which is returned to the vendor for credit.

The reduction-oxidation-reduction sequence mentioned above for the Hanford orange oxide was a development that permits the processing of this material to high levels of conversion to UF_4 at acceptable throughput rates. This orange oxide is produced as spherical particles, and grinding to our required particle size distribution

does not sufficiently open up the particle surfaces for acceptable UF_4 conversion levels. The ROR treatment stresses, strains, and opens the particles so that good hydrofluorination results are obtained.

Another worthwhile improvement in reducing maintenance and keeping the hydrofluorination operation on stream is the successful use of Teflon-lined pipe to carry the reactor off-gases (30% HF, 70% H_2O) to the Karbate condenser system.

Other developments in the hydrofluorination processing which are reported, but which we do not use, include (1) recovery of the dilute HF from the off-gas with recycle to the hydrofluorination system.⁸ and (2) fluid bed reactors for the hydrofluorination step.⁹ Both of these approaches have their merits and can be of interest for particular applications. The conversion of UO_2 to UF_4 is an exothermic and highly reversible reaction, so the mode of operation with respect to temperature and HF- H_2O concentration must receive close attention. Our standard reference data in this area was established by our co-worker, Briggs.^{10, 11}

Green salt must, in addition to having an acceptably low metallic impurities content, have a high UF_4 assay to process properly in subsequent uranium metal operations (see Table II for UF_4 specifications). Ordinarily, only small amounts of UO_2 and UO_2F_2 (<2%) are permissible in the green salt. The UO_2 derives from (1) incomplete conversion in the hydrofluorination operation, (2) thermal damage to the oxide in the reduction of UO_3 , (3) an imbalance in the UO_2 -HF feed ratio, or (4) an improper temperature/HF- H_2O profile

in the hydrofluorination reactors. The UO_2F_2 derives from (1) an inadequate conversion in the oxide reduction step or (2) air inleakage during hydrofluorination. The significance of UO_2 and UO_2F_2 in UF_4 during uranium metal production operations will be discussed below.

Of historical interest was the production of UF_4 by the National Lead Company of Ohio using an aqueous process (WINLO) with uranium residues as the feed;¹² this process was discontinued when techniques were developed for blending these residues into the main Refinery extraction feed system. Another process noted in passing was the moving bed reactor for UF_4 production.¹³

URANIUM METAL PRODUCTION

The production of uranium metal continues by the time-honored process developed by the Iowa State group:

By proper blending and preheating of the ingredients, temperatures are attained by this exothermic reaction such that molten uranium and molten magnesium fluoride slag are present at the end of the short reaction period. Upon cooling, the uranium regulus (or derby, as we call it) is readily separated from the slag mass.

Figure 2 shows the uranium metal production flow diagram. The reaction is performed inside a Cor-ten (high strength, low alloy steel) furnace pot containing a liner of magnesium fluoride slag. This insulating liner is tamped in place around a hollow mandrel on a pneumatically-operated jolter. After the mandrel is withdrawn,

blended UF_4 and magnesium metal powders are charged into the lined furnace pot using a special filling machine. The nearly filled furnace pot is topped with a layer of magnesium fluoride (same material as side liner), then closed by bolting on a steel lid. The charge assembly is then placed in an electrically heated furnace operating at about 1300°F (a thermocouple in contact with the furnace pot mid-wall is used, and the actual temperature used varies according to the nature of the UF_4 being processed). The reaction occurs spontaneously after a heating time of about $3\frac{1}{2}$ hours. The furnace pot is then removed from the furnace, air-cooled for a time, then water-cooled to room temperature. The furnace pot is then upended and jolted to discharge the contents.

The uranium regulus, or derby, is cleaned mechanically, then remelted in an induction-heated vacuum furnace with reject metal from other fabrication operations, and cast into cylindrical ingot molds for subsequent rolling or extrusion into fuel core blanks. These blanks are then precision-machined to final size.

The magnesium fluoride slag and liner are processed through a crushing, screening ball-milling circuit after which part of the material is reserved for future liner material. The rest is treated with nitric acid for recovery of the contained uranium. (For slag containing less than 0.2% ^{235}U , economics favor disposal rather than recovery.) Generally, but not always, the slag and slag liner materials are kept segregated according to the isotopic level being processed.

The isotopic levels of UF_4 currently being processed include:

1. "Near-normal" produced by combining materials which are slightly above and below natural ^{235}U isotopic percentages so that the product approximates the ^{235}U ratio of natural uranium.
2. Slightly enriched ^{235}U materials produced from irradiated fuel reprocessing operations at the nuclear reactor operations, blended with other enriched materials to the desired isotopic level.
3. Depleted UF_4 ($<0.2\%$ ^{235}U) obtained from the AEC inventory associated with the gaseous diffusion operations.

The various UF_4 sources are noted because some changes in operating technique are required to obtain optimum production results with each type. The depleted UF_4 , obtained by hydrogen reduction of UF_6 , has different characteristics than the UF_4 obtained by reduction and hydrofluorination of orange oxide.

Magnesium quality is another important variable in the production of uranium metal. From the early 1950's through 1964, our magnesium was obtained from an AEC contractor, Nelco Metals, Inc., Canaan, Conn., and employed the ferrosilicon process. The ingot magnesium was ground to our particle size requirements by Metals Selling Corp., Putnam, Conn. or Read Manufacturing Co., Lakehurst, N. J. At the suggestion of the AEC, we began evaluation of Nelco cut-crown magnesium¹⁴ in 1964. With the cut-crown magnesium, the magnesium condensate masses from the retort operation are chopped up to a

nominal 6-mesh size without going through the melting and ingot casting steps. Savings in magnesium costs by use of the cut-crown material were significant, but the higher nitrogen and oxygen content had a generally detrimental effect on the uranium metal product. In 1965, we began to review additional sources of magnesium and found that Dow Chemical Company manufactured electrolytic process magnesium which looked promising.¹⁵ A difficult element to control in the electrolytic magnesium process is iron (our upper specification limit at the time was 75 ppm); Dow had produced limited quantities of low-iron magnesium by a patented process involving bubbling of titanium tetrachloride into the molten magnesium prior to casting. A significant cost was incurred in the iron removal step, and, for reasons which have never been fully understood, the magnesium had to be used in our process within narrow limits around the stoichiometric requirement, or damaging pressures were generated during the reduction reaction phase. To make an otherwise long story short, we found that Dow could supply a grade of magnesium containing 250 to 350 ppm iron (Grade 6), and this would be satisfactory for our use¹⁶ provided the range of iron values could be supplied within the 250 to 350 ppm limits; by this time, the use of controlled iron additions to the finished uranium product was an established procedure for metallurgical considerations. This Dow magnesium was phased into production use while the availability of cut-crown magnesium ceased with termination of magnesium metal operations at the Canaan plant. Our current magnesium specifications are given in Table III.

Beginning in 1966, magnesium from the National Stockpile became available for our use. This material was stockpiled in the early 1950's (all ferrosilicon process, low iron content; many more tons electrolytic source, too high in impurities), and our consumption from this source has ranged from Dominion, Somerville, N. J., to Pacific Northwest and Kaiser, Hastings, Nebraska, to, currently, Pacific Northwest, Sharonville, Ohio. Due to the increased requirements for magnesium metal by other consumers, Dow has withdrawn as a supplier for the uranium industry. Alabama Metallurgical Corp., Selma, Alabama has also supplied part of our magnesium requirements in recent years but has recently ceased magnesium production (the last facility in the U. S. using ferrosilicon process). We are hopeful that the magnesium of Pacific Northwest manufacture from the Sharonville Depot will continue to be made available for our use through the coming years.

The uranium tetrafluoride-magnesium reaction has been carried out on a production basis in furnace pots of widely varying sizes. These have ranged in capacity from the equivalent of only a few pounds of uranium (used primarily for highly enriched material) up to the giant "dingot" charge of 3300 pounds of uranium developed by Mallinckrodt.¹⁷ Our standard furnace pot is about 16 inches in diameter and produces about 350 pounds of uranium per charge. A 20-inch furnace pot was successfully developed¹⁸ here. This pushed the existing reduction equipment to its limit and produced 50% more metal per charge. A shortage of capital funds militated against conversion to this larger reduction unit.

A number of other techniques have been investigated for the production of uranium metal. All have been discontinued short of completely successful demonstration. These include (1) an electrolytic process by Mallinckrodt,¹⁹ (2) a pressurized, semi-continuous reduction process by the National Lead Company of Ohio²⁰ using the standard UF_4 -magnesium reactants in powder form, and (3) a process using large briquetted charges²¹ in a standard furnace pot. Here the main problem was the cost of the presses needed for briquette forming.

As was mentioned in the uranium tetrafluoride discussion above, a high-purity UF_4 containing only small percentages of UO_2 and/or UO_2F_2 is required for optimum uranium metal production. The UO_2 , as well as any oxides in the magnesium, is incompletely reduced to metal in the process, and we believe that these oxides generally function as solid emulsifying agents for the molten metal and slag phases (low solubility in both phases) and interfere with a clean separation of the slag and metal at the end of the reaction. We also know that metal which is contaminated with oxide inclusions carries the inclusions through the subsequent remelt and fabrication steps. This results in a high reject rate in the machined uranium fuel cores (nitrogen in the magnesium metal can produce similar effects).

The UO_2F_2 can also serve as an oxide source in the metal reduction step, but its most serious effect is to increase the firing time; that is the time the reduction charge remains in the furnace until spontaneous initiation of the reaction takes place. It is usual practice to vary the furnace operating temperature in order to

realize a target firing time which results in high metal yields and good slag-metal separation. The UO_2F_2 content of the UF_4 also has an effect on the pressure developed during the reaction phase, but the reasons for this are not completely understood. Theoretically, the reaction of UO_2F_2 and magnesium releases more heat than the primary UF_4 -Mg reaction. This could, in turn, result in higher pressure from the excess magnesium in the charge. We also believe that the longer firing times associated with increasing UO_2F_2 levels would serve in a similar manner due to the higher sensible heat at initiation of the reaction phase. The higher pressures may also be the result of UO_2F_2 forming gaseous fluorine compounds (e.g., OF_2).

The green salt produced from the reduction of uranium hexafluoride is essentially pure UF_4 , but it requires attention in metal operations because of other peculiarities. The relative absence of UO_2F_2 tends to result in premature initiation of the reaction; hence furnace operating temperatures must be lowered. The relative absence of magnesium filming agents such as UO_2F_2 also appears to encourage partial reduction of the UF_4 to UF_3 as the preheating continues so that the rate-limiting step, UF_3 to uranium metal, lacks the driving force necessary for high metal yields. This high-purity UF_4 also tends to interact with the magnesium fluoride liner to a greater extent than the other UF_4 types, resulting in a slightly oversize metal regulus and lower yields due to the UF_4 combining with the liner material. To prevent the latter, we have implemented a technique borrowed from Union Carbide at Paducah which involves the uniform spraying of a small quantity of water (0.01%, U basis)

onto the side-wall liner before placing the charge into the lined furnace pot. We have also found that this UF_4 is more sensitive to magnesium excesses than other types and that a relatively uniform application of heat to the furnace pot surface is desirable.²²

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TABLE I

ORANGE OXIDE (UO₃) SPECIFICATIONS FOR THE HYDROFLUORINATION PROCESS

Chemical

UO ₃ assay	97.0% min
NO ₃	1.0% max
H ₂ O	1.6% max

<u>Impurities</u>	<u>ppm (U basis) max</u>
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Chromium	20
Iron	50
Nickel	15
Sodium	25
Thorium	750
Sulfate (SO ₄)	1300 min, 1800 max

Physical

<u>U. S. Sieve No.</u>	<u>Min, %</u>	<u>Max, %</u>
+40	-	2
-80	85	-
-325	50	70

<u>Tap Density</u>	3.8 g/cm ³ min
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TABLE II

GREEN SALT (UF₄) SPECIFICATION FOR URANIUM METAL PRODUCTION

Chemical*

UF ₄ assay	96.2% min
UO ₂	2.0% max
UO ₂ F ₂	1.8% max
H ₂ O	0.05% max

<u>Impurities</u>	<u>ppm (U basis) max</u>
Chromium	40
Copper	80
Iron	75
Nickel	80

* The physical characteristics of UF₄ are essentially fixed by the parent UO₃ and are not specified.

TABLE III

MAGNESIUM METAL SPECIFICATIONS FOR USE IN URANIUM METAL PRODUCTION

Chemical

Magnesium	99.8% min
<u>Impurities</u>	<u>ppm, max</u>
Aluminum	300
Boron	0.3
Cadmium	1.0
Chromium	50
Copper	200
Iron	75
	(or 250 min, 350 ppm max)
Manganese	75
Nitrogen	200
Nickel	50
Silica	250
Zinc	300
Zirconium	100
Others, each	100*

Physical

<u>U. S. Sieve No.</u>	<u>Percent</u>
+10	2 (max)
-10 +20	50 to 66
-20 +30	26 to 40
-30 +40	3 to 10
-40 +50	1 to 3
-50	2.5 (max)
-120	0.2 (max)

* Except oxygen and calcium which shall be included in the total impurity content maximum of 2000 ppm (0.2%) in order to maintain the 99.8% minimum magnesium content.

Figure 1 Uranium-Tetrafluoride Production Flowsheet

Figure 2 Uranium Metal Production Flowsheet