

# CERAMIC UO<sub>2</sub> POWDER PRODUCTION AT CAMECO CORPORATION

### A.K. KWONG and S.M. KUCHUREAN

Cameco Corporation Port Hope, Ontario

#### ABSTRACT

This presentation covers the various aspects of ceramic grade uranium dioxide  $(UO_2)$  powder production at Cameco Corporation and its use as fuel and blanket fuel for heavy-water and lightwater reactors, respectively.

In addition, it discusses the significant production variables that affect production and product quality. It also provides an insight into how various support groups such as Quality Assurance, Analytical Services, and Technology Development fit into the quality cycle and contribute to a successful operation. The ability of Cameco to identify, measure and control the physical and chemical properties of ceramic grade  $UO_2$  has resulted in the production of uniform quality powder. This has meant that 100% of Cameco's ceramic grade  $UO_2$  powder produced since mid-1989 has been accepted by the fuel manufacturers.

# **1.0 INTRODUCTION**

Cameco Corporation is the world's largest publicly traded uranium company and a growing gold producer. Currently, Cameco conducts an aggressive exploration program in Canada, the United States, Central Asia and Australia to support the corporation's long term objective of maintaining its status as an integrated leader in the nuclear industry and a recognized gold producer.

Cameco's Canadian Operations include the world's two largest high-grade uranium mines, Rabbit Lake and Key Lake, in Saskatchewan, and uranium refining and conversion facilities in Ontario. It has uranium and gold mining operations in Saskatchewan, uranium processing facilities in Ontario and a gold mine in Kyrgyzstan in Central Asia. Through its wholly owned producing subsidiaries, Cameco obtains uranium from operations in Wyoming and Nebraska.

Cameco plays a major role in the nuclear fuel cycle by supplying fuel for both heavy-water and light-water reactors. It has a modern refining facility in Blind River, a small community in Northern Ontario and a modern conversion complex in Port Hope, a small town on the north shore of Lake Ontario and approximately 100 km east of Toronto. In the Blind River Refinery,

uranium mine concentrates are converted to pure uranium trioxide  $(UO_3)$  powder, used as feed material for the Port Hope Conversion Facility. The UO<sub>3</sub> produced is packaged in tote bins for shipping. In the Port Hope Conversion Facility, approximately 80% of the UO<sub>3</sub> is converted to uranium hexafluoride (UF<sub>6</sub>) which is exported to enrichment plants abroad and subsequently used to fuel light-water reactors. The remaining 20% is converted to ceramic grade UO<sub>2</sub> powder as fuel for CANDU reactors and as blanket fuel for light-water reactors.

Ceramic grade  $UO_2$  powder has been produced at the Port Hope Conversion Facility since 1958. Production in the early days was batchwise, limited to a few tonnes per year and the original  $UO_2$  technology has gone through numerous significant changes. The current ceramic  $UO_2$  plant is modernized with computer monitoring and control which allows plant operations personnel to view real time and historical data using a fully integrated control system. Today, Cameco has positioned itself with the ability to supply ceramic grade  $UO_2$  powder to fulfill customer needs in terms of quality and quantity for domestic and international use as CANDU or blanket fuel.

### 2.0 URANIUM PRODUCTION

Cameco's uranium business consists of exploration, mining, refining and conversion of uranium for sale as an intermediate and final product in the manufacturing of nuclear fuel.

#### 2.1 Mining

Cameco owns the world's two largest high-grade uranium mines, Rabbit Lake and Key Lake in Saskatchewan. Its total 1996 Canadian triuranium octoxide  $(U_3O_8)$  production was 16.6 million lbs (7.5 million kg) or 18% of the world's production. In addition to its Canadian mines, Cameco also obtains uranium from its wholly owned American subsidiaries in Wyoming and Nebraska, Power Resources Inc. and Pathfinder Mines Corporation. Cameco's total US production of  $U_3O_8$  is now more than 1.7 million lbs (0.7 million kg).

Cameco has recently received approval from the Atomic Energy Control Board of Canada to operate the McArthur River Project and is seeking approval for the Cigar Lake Operation. In both sites, Cameco is the majority stake holder and operator. The grade of ore at these two sites will exceed those of Rabbit Lake and Key Lake operations by a factor of 10. For example, the typical grade of ore produced at Rabbit Lake and Key Lake is  $1.5\% U_3O_8$  while the typical grade of ore produced at McArthur River is expected to be  $12 - 18\% U_3O_8$ .

## 2.2 UO<sub>3</sub> Production

Cameco has the world's most modern uranium refining facility in Blind River, Ontario. It receives drums of uranium ore concentrate from mines in Canada, Australia, the United States, Africa and many other countries. Uranium is separated from impurities contained in the mine concentrates in a refining process using digestion, solvent extraction, denitration and other processes. The result is a nuclear grade uranium product known as UO<sub>3</sub>. All UO<sub>3</sub> produced at

the Blind River Refinery is shipped to the Port Hope Conversion Facility in tote bins where it is converted to  $UF_6$  and ceramic grade  $UO_2$  powder.

#### 2.3 UF<sub>6</sub> Production

In the Port Hope Conversion Facility, approximately 80% of the UO<sub>3</sub> produced in Blind River is converted to UF<sub>6</sub> which is exported to enrichment plants abroad. Currently, Cameco supplies approximately 25% of the global UF<sub>6</sub> market. The remaining 20% of UO<sub>3</sub> is converted to ceramic grade UO<sub>2</sub> powder.

The production of  $UF_6$  involves several process steps:

- (a) Reduction: Pulverized  $UO_3$  powder is reduced to  $UO_2$  in a two stage fluidized bed reactor with hydrogen.
- (b) Hydrofluorination:  $UO_2$  powder is converted to uranium tetrafluoride (UF<sub>4</sub>) slurry in a series of stirred tank reactors with anhydrous and aqueous hydrofluoric acid. The UF<sub>4</sub> slurry is then dried and calcined in a double drum dryer and calciner to remove all free and hydrated water.
- (c) Fluorination:  $UF_4$  powder is reacted with fluorine in a flame reactor to produce gaseous  $UF_6$ . The  $UF_6$  gas is filtered, condensed, liquefied and then fed into shipping cylinders.

### 3.0 CERAMIC UO<sub>2</sub> POWDER PRODUCTION

Cameco is an industry leader in the production of ceramic grade  $UO_2$  powder for both natural and depleted. With almost forty years operating experience, Cameco has refined its ceramic  $UO_2$ technology and optimized its production facilities to position itself with the ability to fulfill its customers' requirements in terms of quality and quantity for both CANDU and blanket fuel.

#### 3.1 Ammonium Diuranate (ADU) Process

The production ceramic grade  $UO_2$  powder consists of five processing steps as presented in the following sections. A schematic process flow diagram for ceramic UO2 powder production is given in Figure 1.

**Dissolution**:  $UO_3$  powder is dissolved in an agitated tank with nitric acid to form uranyl nitrate (UN) solution. The specific gravity, free acid strength and temperature of the UN solution are controlled to specific set points to ensure all  $UO_3$  particles are dissolved. Fume collection is provided at the tank to prevent nitric acid vapours from escaping into the plant. When the batch has met the specific gravity and free acid control points, it is manually pumped to a storage tank.

**Precipitation**: In this process step, concentrated UN is transferred to a dilution tank where it is automatically diluted with process water to a controlled specific gravity and temperature. The diluted UN solution is transferred to a precipitation tank where it reacts with aqueous ammonia to form ADU precipitate. After the reaction is complete, the ADU is allowed to settle and the

ammonium nitrate ( $NH_4NO_3$ ) solution is decanted to a treatment circuit. The ADU slurry is drained to a storage tank for the next processing step. In the treatment circuit, the  $NH_4NO_3$  is concentrated, purified and sold to a local fertilizer manufacturer.

**Drying**: The ADU slurry in the storage tank is maintained at a predetermined temperature and pumped to two centrifuges for liquid-solid separation. The centrate, mostly dilute  $NH_4NO_3$  solution is sent to the  $NH_4NO_3$  treatment circuit and the ADU cake is discharged to a tray dryer where the moisture is removed. The dry ADU powder is transferred to a surge bin via a screw conveyor and a bucket elevator.

**Reduction**: Dry ADU powder is fed to rotary kilns, operating in parallel, where it is reduced to  $UO_2$  powder by reaction with hydrogen in a counter current flow. The rotary kilns are heated with natural gas and kiln temperatures are automatically controlled to allow proper and complete reduction. The reduced  $UO_2$  powder is passed through a conditioner where it is stabilized and cooled to a predetermined temperature before discharging into 45 gallon drums.

The  $UO_2$  powder produced is homogenized in a double cone blender, sampled and certified prior to shipping to fuel manufacturers.

 $NH_4NO_3$  Treatment:  $NH_4NO_3$  solution is a by-product in the production of ammonium diuranate and is sold to a fertilizer manufacturer after going through a treatment circuit which consists of the following steps:

- (a) Filtration: To remove particulates.
- (b) Concentration: To evaporate the dilute  $NH_4NO_3$  solution to a predetermined specific gravity to provide sufficient nitrogen content for fertilizer manufacturing.
- (c) pH Adjustment: To precipitate all uranium from solution by the addition of aqueous ammonia and a coagulant.
- (d) Final Filtration: To remove particulates from the  $NH_4NO_3$  solution.
- (e) Certification: After a storage tank is filled, the  $NH_4NO_3$  solution is sampled, analysed and certified prior to shipment. The last annual average uranium concentration in the  $NH_4NO_3$  reported, August 1996, to Agriculture and Agri-food Canada was  $\leq 2.0$  mg/L.

## **3.2 Process Control**

The physical characteristics of ceramic grade  $UO_2$  powder depend on, to a large extent, the precipitation conditions of ADU and, to a lesser degree, the reduction conditions. Therefore, there has been much effort spent on controlling the following operating parameters:

- (a) Concentration of ammonium hydroxide solution;
- (b) Specific gravity, free acid and temperature of the UN solution;
- (c) Consistency of ADU cake after solid-liquid separation;
- (d) Reduction Temperature.

The dissolution of anhydrous ammonia is controlled automatically with a density meter.

However, difficulties in controlling the aqueous ammonia strength to a narrow range are frequently experienced. It is believed that the strength of aqueous ammonia directly affects the particle size of ADU and consequently the sintered density and specific surface area of ceramic  $UO_2$  powder. It is because of the slight variations of aqueous ammonia strength, the physical characteristics of  $UO_2$  powder, e.g. sintered density, specific surface area and bulk density, differ slightly from day to day.

The specific gravity and temperature of the uranyl nitrate solution also influences the filterability of ADU slurry, and the sintered density and specific surface area of the resulting  $UO_2$  powder. It has been observed that an elevated uranium concentration and temperature condition during the precipitation process may produce an ADU slurry with poor filterability characteristics. This condition may produce  $UO_2$  powder with low specific surface area and sintered density characteristics. The ADU precipitation process was automated in the early 90's to eliminate the variability of those process parameters. Since then the results have been excellent and consistent as indicated in Figure 2.

The consistency of ADU cake after solid-liquid separation has a direct impact on the specific surface area and sintered density of  $UO_2$ . Normally, a drier ADU cake will result in higher specific surface area and sintered density  $UO_2$  powder. The consistency or dryness of the ADU cake is manually controlled by the operator. When the ADU dryer temperature starts to fall, the operator will initiate actions such as cleaning the centrifuge cloth and increasing the monitoring of the ADU slurry temperature, ADU dryer heaters and ADU precipitation conditions. Since the automation of the ADU precipitation process, the dryness of the ADU cake has been consistent due to the steady conditions of the ADU slurry feed to the centrifuge.

Reduction temperature has a minor influence on  $UO_2$  powder characteristics when it is controlled within a range of 35°C. Abnormal elevated temperatures over 750°C will reduce the specific surface area and sintered density. On the other extreme, with temperatures below 600°C, incomplete reduction will occur. The bed temperature of the reduction kilns is controlled automatically and monitored closely by the operators.

#### 3.3 **Production Specifications**

As stated earlier, Cameco supplies ceramic grade  $UO_2$  powder for use in domestic and offshore CANDU reactors and for use as blanket fuel in light water reactors. Cameco has two specifications for its natural ceramic grade  $UO_2$  powder production, namely Cameco Specification (CS)-1 for CANDU fuel and CS-2 for blanket fuel. Moreover, because of its advanced ceramic  $UO_2$  technology and its production capability, Cameco can tailor-make ceramic grade  $UO_2$ powder to meet a customer's unique requirements. In addition to the production of natural ceramic  $UO_2$  powder, Cameco also produces depleted ceramic grade  $UO_2$  powder to specification CS-3.

#### 3.3.1 Cameco Specification (CS)-1

CS-1 was developed specifically to meet the needs of the CANDU fuel customers and the Atomic Energy of Canada Limited's TS-XX-37032-001. A list of the impurities and the corresponding maximum levels is given in Table 1. Cameco's ceramic grade  $UO_2$  powder has not only consistently met the CS-1 specification, but has been significantly below the maximum allowable levels. Referenced Table 1 for 1996 average production results. Figure 2 also illustrates the average  $UO_2$  sintered density and specific surface area from 1985 to 1996.

#### 3.3.2 Cameco Specification (CS)-2

CS-2 was developed to meet the needs of blanket fuel customers. The significant difference between CS-1 and CS-2 is the maximum impurity level for thorium has been reduced from 500 ppm to 10 ppm uranium basis. The other minor differences include the reporting of several other elements such as nitrogen, lead, tin, vanadium, tungsten, zinc, and thorium 230. A list of the impurities and the corresponding maximum levels are given in Table 1.

# 4.0 TECHNICAL SUPPORT

Cameco is committed to producing consistent and superior quality products in a most cost effective manner. The production of ceramic grade  $UO_2$  powder is a good example of this firm commitment.

The production of ceramic grade  $UO_2$  powder involves a team of professionals from various departments working closely to ensure quality assurance programs are strictly followed and product qualities meet or surpass customer specifications. Production processes are continually reviewed to identify potential areas for improvement in safety, environment, quality and production practices. The following paragraphs describe briefly the support groups involved and their corresponding roles and capabilities.

The Analytical Services group provides analysis and certification of  $UO_2$  powder prior to shipment. It also carries out periodic analysis of chemicals to ensure suppliers are in conformance to Cameco specifications. A wide range of analytical instrumentation is used, namely, Inductively Coupled Plasma - Mass Spectrum (ICP-MS); a Wavelength Dispersive X-ray Fluorescence Spectrometer (WDXRF); and, an Atomic Absorption Spectrophotometer (AAS). Chemically, the Analytical Services group is able to analyse impurities down to sub ppm levels. It has a laboratory in the  $UO_2$  plant to provide daily determinations of  $UO_2$  particle size, specific surface area, bulk, green and sintered density.

The Quality Assurance Group is responsible for the maintenance of Cameco's Quality Assurance program. It conducts periodic audits of the production operation to ensure the Quality Program is strictly adhered to. The Quality Program is designed to ensure that the customer's quality requirements are recognized and met. It is also designed to satisfy the requirements of CSA Standard Z299.2 (1985) and other equivalent standards. It is also located in the UO<sub>2</sub> plant, which permits easy discussions for matters that may arise pertaining to the quality of the  $UO_2$  powder.

Technology Development, formerly Research and Development, consists of a group of highly qualified scientists, engineers and technologists. In addition to people resources, it has a well equipped diagnostic facility containing a wide spectrum of scientific instruments. This group is involved in the characterization of ceramic  $UO_2$  powder and the correlating of production conditions to  $UO_2$  powder characteristics. In addition, it is involved in the development of new processing technologies as well as providing technical support to customers.

In conclusion, Cameco is the industry leader in the production of ceramic grade UO2 powder. It has the most advanced  $UO_2$  technology and production capabilities. In addition, Cameco is a very progressive company and is fully committed to providing, on a long-term basis, outstanding value to our customers.

#### ACKNOWLEDGEMENTS

The authors wish to thank Mr. T.W. Kennedy, Mr. Engin Ozberk, Mr. W.M. Crawford, Mr. J.S. Friedmann and Mrs. Hailing Liu, Ph. D. for their support and contribution to writing this paper. Special thanks are also extended to analytical, quality, production and technology development groups for their commitment to making Cameco a leader in supplying ceramic uranium dioxide powder to the domestic and international markets.

## REFERENCES

1. R.T. Tanaka and T.W. Kennedy, "History of UO<sub>2</sub> Production at Port Hope", International Conference on CANDU Fuel, October, 1986.

# TABLE 1

# SUMMARY OF CAMECO UO<sub>2</sub> SPECIFICATIONS

ELEMENT	SYMBOL	CAMECO SPECIFICATIONS		TYPICAL SPECIFICATION	CS-1 '96
	5111202	CS-1	CS-2	FOR BLANKET FUEL	AVERAGE
Aluminum	Al	25	25	30	< 5
Boron	В	.3	.3	0.5	0.1
Carbon	C	200	100	150	80
Calcium	Ca	50	50	25	5
Cadmium	Cd	0.2	0.2	0.5	< 0.2
Chromium	Cr	15	15	100	9
Соррег	Cu	10	10	25	1
Dysprosium	Dy	0.15	0.15	0.1	< 0.05
Fluorine	F	30	30	50	5
Iron	Fe	75	70	100	40
Gadolinium	Gd	0.1	0.1	0.1	0.02
Magnesium	Mg	10	10	50	1
Manganese	Mn	5	5	25	1
Molybdenum	Мо	2	2	25	0.6
Nickel	Ni	20	20	100	5
Silicon	Si	30	30	100	< 10
Thorium	Th	500	10	50	< 5
Phosphorus	Р	35	35	50	20
Sodium	Na	20	20	100	5
Potassium	K	20	N/S	N/S	10
Silver	Ag	N/S	1	0.3	N/A
Chlorine	Cl		15	15	
Cobalt	Co		35	75	
Nitrogen	N		75	75	
Lead	Pb		50	10	
Tin	Sn		50	10	
Thorium 230	Th 230		0.001	N/S	
Vanadium	V		50	10	
Tungsten	W	N/S	50	50	N/A
Zinc	Zn		50	50	

NOTE: Impurity concentration identified as mg/gU.

195





# FIGURE 2

# **UO2 PRODUCTION : 1985 - 1996**

CS -1 Lots



--- SD ---- SSA

I

)

]

. ]

ļ

. ]

J

J

J

197

I

ł

1

. ]