NEW PROCESS FOR NATURAL URANIUM BY-PRODUCT PREPARATION IN URANIUM REFINING OPERATIONS

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ABSTRACT

Cameco Corporation's conversion operations are located in Ontario, Canada with a uranium refinery located in Blind River. The refinery produces commercial natural uranium trioxide (UO_3) from uranium ore concentrate (UOC) which is received from mines throughout the world. The UO_3 product is transported by road in bulk containers to the conversion facility in Port Hope for processing to ceramic grade uranium dioxide (UO_2) to supply CANDU fuel customers, or to uranium hexafluoride (UF_6) for the light water reactor fuel cycle.

INTRODUCTION

The refining process which is carried out at Blind River utilizes nitric acid digestion followed by solvent extraction. The solvent used in the process is tributyl phosphate in a kerosene diluent. The stripped aqueous stream from the extraction process is referred to as raffinate. The raffinate is an aqueous slurry of nitric acid and the impurities, mostly metal nitrates, which were rejected from the solvent extraction process. The raffinate also contains low concentrations of uranium, typically <1.0 g/L. In the past, the raffinate was concentrated in steam heated evaporators to remove most of the water and nitric acid from the raffinate. Sulphuric acid was added to convert the metal nitrates into metal sulfates and for the recovery of the remaining nitrates as nitric acid and mixed gaseous oxides of nitrogen, NO and NO_2 (NOx). The concentrated and sulfated raffinate was then shipped by road tanker to a uranium mining operation in Elliot Lake, Ontario as a uranium by-product slurry for processing in the mill to recover uranium. See figures 1 and 3 (attached).

With the closure of the Elliot Lake mines in the early 1990's, it was necessary for Cameco to develop a new process for the handling of raffinate. Through extensive piloting and design work, a process was developed to convert concentrated raffinate into a dry product which could then be denitrated at high temperatures using a calciner. The objective of this project was to prepare a free flowing metal oxide powder which is stable for transport and suitable for recycling as a by-product at a uranium mill. See figure 2 (attached).

CONCENTRATED RAFFINATE PREPARATION

The existing two stage dilute raffinate evaporators continue to be used for the first step in by-product preparation. These evaporators consist of horizontal shell and tube heat exchangers with overhead flash chambers for vapour disengagement. The highly concentrated raffinate which is produced in this process step has a higher viscosity than that of the original sulfated raffinate. The viscosity of the by-product slurry in the second stage evaporator increased from an average of 3,500 cP to greater than 20,000 cP. To prevent fouling of the second stage heat exchanger tubes with the higher viscosity raffinate, the circulating pump impellor diameter was increased from 15 inches to 18 inches to maintain an adequate flow velocity. This larger impeller causes cavitation problems when the density of the raffinate falls below 1.6 kg/L; thus it is necessary to start the evaporator with concentrated product.

Sulphuric acid is used in the evaporation process to convert alkali nitrates to sulfates, which allows the downstream denitration process to operate at lower temperatures. Most of the time sufficient amounts of sulfuric acid are available in the raffinate due to the sulfate content of the UOC which is processed.

The concentrated raffinate from the evaporator is pumped to insulated surge tanks and from there to drum dryers using rotary disc centrifugal pumps suitable to handle high viscosity slurries.

RAFFINATE DRYING

Three steam heated double drum dryers are utilized to convert the concentrated raffinate slurry into a dry product containing mostly metal nitrates. Each dryer unit consists of two drum rolls heated with steam, a feed dip tray, a variable speed drive, two knife blades and two discharge screw conveyors.

The drum rolls pick up the raffinate from the slurry dip tray, shaped as an inverted pyramid, with the feed nozzle at the apex. The raffinate slurry level in the tray is maintained by two fixed overflow weirs which ensure that the drum rolls are submerged in the slurry. The feed rate to the dryer dip tray is 5,900 kg/h (3.2 m^3/h). To prevent a build up of solids in the tray, the excess feed overflows from the dryer tray back to the concentrated raffinate feed tank. Dry raffinate is produced from a drum dryer at a rate of about 350 kg/h.

The stainless steel rolls for the drum dryers are rated for 200 psig steam, but operate at 150 psig. The higher steam pressure rating is to allow for corrosion or wear on the drum roll. The operating temperature of the drum roll is 182^{o}C, with a product discharge temperature of 158^{o}C. The water and nitric acid in the concentrated raffinate are evaporated at a rate of approximately 245 kg/h. The dry raffinate produced is a metal nitrate powder with a moisture content of less than 3.0%, and a nitrate content of 7.5% as N. The moisture content of the product is controlled by the rotational speed of the rolls and the density of the concentrated raffinate feed. If the moisture exceeds 5.0%, the product forms a paste which is difficult to handle and plugs the flygts of the product transfer conveyors.

The knife blades used to remove the dry raffinate from the drum surface are fabricated from 440C grade stainless steel and are heat treated to provide a steel with adequate hardness. The blades are typically used for approximately 96 hours before they have to be removed and sharpened. Sharpening the blades does reduce the subsequent life cycle due to the reduction in their width. The angle of the blade on the drum surface must be maintained at 22.5-24^{o} in order to provide the proper scraping of the drum. If the angle is less than 22.5^{o} the blade will flex away from the drum and ride on the surface layer of dry raffinate. If the angle of contact is greater than 24^{o} the blade will gouge the drum surface. Any buildup of dry raffinate on the drum dramatically reduces heat transfer and throughput.

DENITRATION

The dry raffinate from the drum dryers is temporarily stored in the calciner feed bin prior to processing in the calciner. The feed bin is a stainless steel hopper with a surge capacity of 3.0 m^3. Bin hammers mounted on the sloped bin bottom assist the flow of the dry raffinate to the bottom and into a variable speed screw conveyor mounted at the bottom. The screw conveyor metres the dry raffinate into the calciner. The variable speed drive is controlled by a PLC which is capable of transferring dry raffinate feed to the calciner at a rate of 474 kg/h. The flygts on the feed screw are tapered from the discharge end to the feed end to reduce the thrust loading on the drive bushing seat. This has also helped to prevent any dust leakage at the drive shaft.

An indirect gas fired rotary calciner is used for the thermal decomposition (denitration) of the raffinate. The calciner discharge is a mixture of metal oxides and metal salts which is identified as calcined by-product (CBP). The calciner tube is 30 inches in diameter and 36 feet in length. Inconel was used as the material of construction to improve the corrosion resistance of the tube. The feed conveyor extends into the calciner feed breech by 2 feet, but is outside of the heated zone. The heating chamber or furnace is 24 feet in length and contains ten natural gas burners, which are divided into three zones for heating. The total heat capacity of the kiln is 5,500,000 BTU.

The combustion gases from the furnace pass through heat recuperators to pre-heat the combustion air for the burners. The temperature of the flue gas exiting the heat recuperators is over 600^{o}C. In order to protect the exhaust blower from excess temperatures, dilution air is drawn into the flue gas stream. The blower then discharges directly to a stack.

The calciner is set at a decline of 1^{o}. This can be varied from 0^{o} to 3.0^{o}. The rotation of the calciner tube is adjustable from 1.5 rpm to 5.0 rpm via a variable speed drive. Lifters on the tube shell provide homogenization of the product. This helps to ensure that dry raffinate has maximum contact with the surface of the tube. The minimum retention time required for the raffinate to completely denitrate is approximately 20 minutes. With an angle of 1.0^{o} and a speed of 3.0 rpm the estimated retention time is 35 minutes.

Decomposition of the nitrates begins at 300^{o}C, with complete denitration at 650^{o}C. The original design of the calciner allowed for a maximum operating temperature of 575^{o}C, but with varying metal nitrate composition, it has been necessary to increase the upper temperature limits to 650^{o}C. The predicted safe design limit for the Inconel tube is 850^{o}C. Product temperature is measured and controlled by a single thermocouple located 3 feet from the discharge end of the tube. NOx formation begins within the first 4 feet of the feed breech or in the Zone 1 control region. The Zone 2 control acts as the main denitration zone with the final section or Zone 3 providing the final denitration.

The calciner seals are flexible stainless steel bellows with graphite faces. To prevent corrosion or deterioration of the seal faces an air purge is injected at four points on each seal. The air addition is regulated at 25 L/m to each seal which is sufficient to prevent NOx or solids from contacting the seal faces.

FUME REMOVAL AND NITRIC ACID RECOVERY

The nitric acid vapours from the dryers and the NOx fumes from the calciner are processed by filtration and a multiple scrubber system. Approximately 255 kg/h of NOx is generated by the denitration process in the calciner. The fumes are passed through a stainless steel sintered metal filter to remove any entrained dust from the gas phase. Cooling of the fumes takes place in an in-line water cooled heat exchanger prior to treatment of the fumes. Initial cooling is required because of temperature limitations of the calciner off-gas blower and the seal on the blower. This blower acts as a booster blower for the fumes leaving the calciner which are then discharged via a venturi scrubber into a direct contact quench column. The quench column has four cone type spray nozzles spraying scrubber acid into the NOx gases thereby reducing gas temperature from 280^{o}C to 110^{o}C. The nitric acid generated in the quench column is recirculated to the first stage venturi scrubber system.

The fumes from the quench column and the drum dryers are passed through direct contact venturi scrubbers to a scrubber surge tank. The fumes from the dryers are generated at a rate of approximately 244 kg/h and consist of HNO_3 and water vapour. The quench column contributes 292 kg/h of NO_2, O_2, NO_3 and water vapour. There is 377 kg/h of condensed water and nitric acid recycled back to the process from the first stage scrubber. The combined gas flow from the first stage scrubbers passes through two more venturi scrubbers which are part of the second stage scrubber package. This combined stream is 195 kg/h of NO_2, O_2, N_2 and water vapour, which is converted into 126 kg/h of HNO_3 and condensed water vapour with a final off gas of 150 kg/h NO_2, N_2, and O_2. The second stage scrubber gases are further processed in the existing nitric acid absorbers where remaining NOx gases are converted into nitric acid which is recycled in the refining process.

CALCINED BY-PRODUCT HANDLING

The calcined by-product discharged from the calciner is transferred to a bucket elevator via an inclined cooling conveyor. The cooling conveyor is a solid flygt style unit with a water cooled external jacket. The cooling conveyor was installed to reduce the temperature of the calcined by-product to protect the bag house dust collector used for the removal of dust from the materials handling equipment. Experience to date indicates that the calcined by-product has a sufficiently high heat transfer coefficient that the temperature of the dust is well within acceptable limits for the fibreglass reinforced cloth filter bags used in the dust collector.

The calcined by-product is transferred from the cooling conveyor to a storage bin via a vertical chain driven bucket elevator. The bucket elevator discharges into a 25 m^3 stainless steel storage tank with a conical bottom. Below the storage tank is an automated drum filling station where recycled uranium ore concentrate drums are filled with calcined by-product. The drum filling station is completely enclosed with an independent dust collection system. A 14 inch diameter rotary feeder is activated when an empty drum is elevated into place below the feeder. The feeder is on a timer which is set to fill the drum to within 7-8 cm of the top edge. The roller conveyors are utilized to transfer the drums to and from the drum filling station. Once the drums are discharged from the filling station they are weighed at a roller conveyor scale. The drums are then assembled into 22 drum lots. Five randomly selected drums per lot are sampled to provide representative lot analysis. Each lot sample is analysed for nitrate (NO_3) and uranium content as well as bulk density. Every fifth lot is analysed for metals.   The composition for CBP is shown in table 1 (attached).

The drummed calcined by-product is inventoried on an outside storage pad, prior to shipping.

CONCLUSIONS AND IMPLICATIONS

This process was commissioned in 1996 and further optimized in 1997. It is currently operating to produce drummed by-product at the Blind River Refinery. Work is continuing to evaluate the process for improved efficiencies and reduced costs.

KEY WORDS

by-product, uranium conversion, uranium refining, solvent extraction

Table 1 - Typical Calcined By-product Composition

Analysis	**%**	**%, dry basis**
H_2O	<1	
NO_3 , as N		<0.1 - 1.0
C		<0.2
SO_4 , as S		1 - 12
NH_3 , as NH_4		<0.1
Si		2 - 4
Mg		1 - 5
Fe		<1 - 8
Ca		2 - 6
Na		15 - 20
K		0.5 - 1.5
U		0.5 - 9
Th		1 - 5
F, Cl, Br, I		<0.5
Cr, Zn, Pb, V, Ti, Bi, Mn		<2
Cu, Ni, Ce, Cd, Sn, Sb, As		<1
Mo		0.5 - 1.0
^{226}Ra		<10 **(Bq/g)**

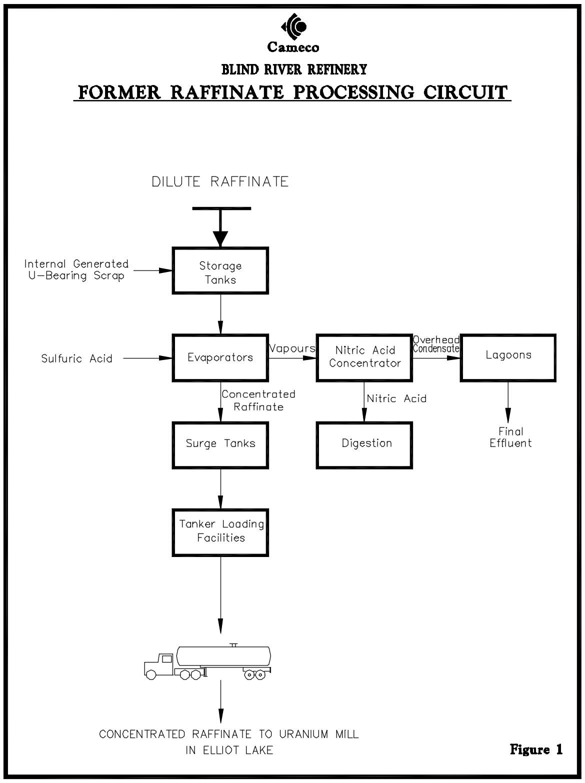

Figure 1

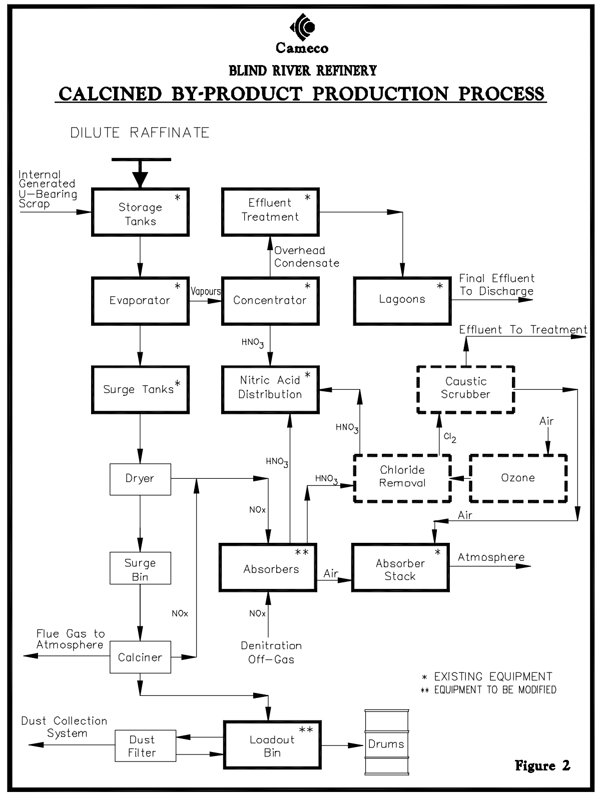

Figure 2

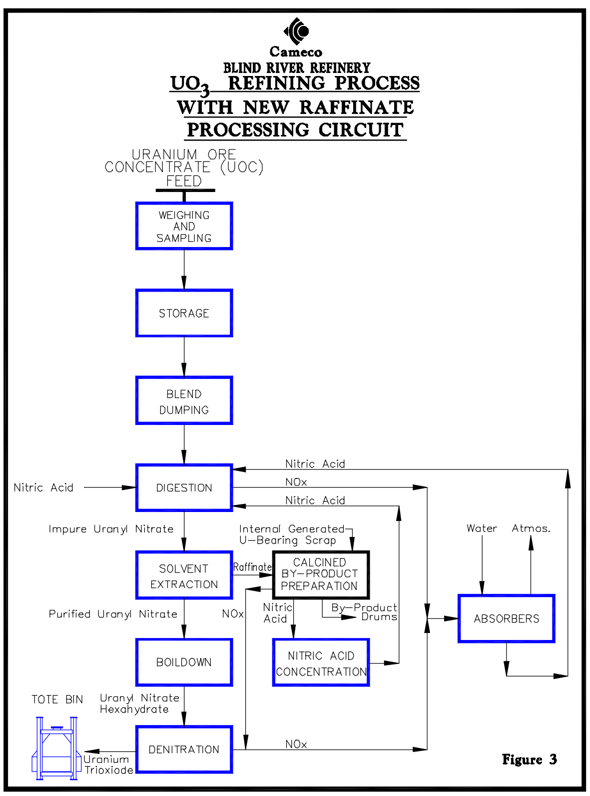

Figure 3