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ABSTRACT

The end of the cold war produced large amounts of excess fissile materials in the United States and Russia. The Department of Energy has initiated numerous activities to focus on identifying material management strategies for disposition of these excess materials. To date, many of these planning strategies have included isotopic dilution of highly enriched uranium as a means of reducing the proliferation and safety risks.

Isotopic dilution by dry blending highly enriched uranium with natural and/or depleted uranium has been identified as one non-aqueous method to achieve these risk (proliferation and criticality safety) reductions. This paper reviews the technology of dry blending as applied to free flowing oxide materials.

INTRODUCTION

One of the most significant challenges before the Department of Energy (DOE) is the development of a complex-wide management program for excess fissile material and related nuclear wastes that meets our national and international policy needs. These policy needs include issues related to nonproliferation, safeguards and security, environmental surety, cost schedule, and nuclear safety. The end of the cold war has reduced processing capabilities across the DOE complex and at the same time generated a large inventory of excess fissile materials in many different physical forms that are in need of stabilization and/or disposition path definition. With uranium these forms include, but may not be limited to, solutions, oxides, compounds, metals, residues, alloys, and fabricated fuel.

Highly enriched uranium (HEU), that is uranium greater than 20% ^{235}U, in any of its physical forms is a primary concern because of proliferation issues and criticality safety issues. These issues were identified in the Defense Nuclear Facility Safety Board's *Recommendation 94-1* and in the DOE's *HEU Vulnerability* study.

The HEU *Environmental Impact Statement* Record of Decision (ROD) selected the disposition path for high quality HEU to be isotopic dilution with natural uranium (NU) and/or depleted uranium (DU) to make low enriched uranium (LEU), for sale as feedstock for commercial nuclear fuel manufacture. The remaining "off-specification" HEU will also be diluted and will be used as "off-spec" LEU feedstock for the Tennessee Valley Authority Light Water Reactor fuel fabrication program.

Under the same ROD, U that can not be dispositioned into LEU feedstock is to be disposed as waste once its ^{235}U enrichment is diluted to 0.9% to further preclude proliferation and essentially eliminate criticality concerns for long-term disposition scenarios i.e., repository disposal. It is anticipated that disposal of this material could occur in a low-level waste disposal complex.

The "off-spec" HEU has high isotopic inventories of ^{232}U, ^{234}U, and ^{236}U. The decay daughters of ^{232}U (i.e., ^{208}Tl) emits high-energy (2.6MEV) gamma radiation and therefore typically requires radiation protection features such as shielding and remote handling.

The HEU in storage at the Idaho National Engineering and Environmental Laboratory (INEEL) is in many forms but the majority of the inventory is in the form of oxides, particularly "off-spec" UO_3. About 1,700 kg of this material is stored in a vault awaiting disposition.

A laboratory-scale project has been completed to test a concept for dry milling and blending of oxides using a patented milling technology. The technology is based on the principle of a planetary ball mill operation and uses novel but simple mechanical principles to effect and vary the centrifugal field and mill rotation. This novel design enables the mill to operate with minimal grinding media at very high centrifugal fields not possible with other milling processes. Due to the enormous centrifugal field, particle size reduction to ultra-fine sizes occurs much faster than with conventional mills and the low amount of grinding media allows for more feed material to be loaded in each batch operation.

Feasibility testing with surrogate materials (titanium monoxide blended with titanium dioxide) has produced excellent mixing results. Size reduction to sub-micron particles is accomplished in a matter of an hour. To date, no physical method of reversing the blending has been identified, and the concept has also received a favorable security/proliferation review from Los Alamos National Laboratory.

THEORETICAL BACKGROUND

Blending is accomplished by a combination of mill action and size reduction of particles. As the grinding occurs, particle size is reduced with a corresponding increase in the number of particles. Uranium oxide with a bulk density of 2.7 gm/cc and an average particle size of 70 microns results in approximately 9.1×10^5 particles/cc. If the average particle size were reduced during grinding to 0.5 microns, the number of particles would increase exponentially to approximately 2.5×10^{12} particles/cc. An increase in the number of particles by two million times, blending action provided by the agitation of the grinding medium and the rotation of the mill all work together to ensure good blending of the powders. This blending and size reduction will make the separation of the HEU from the DU extremely difficult.

Another phenomenon that takes place during dry grinding that adds to the difficulty of separation is the process of mechanofusion. This phenomenon is well understood and is exploited in milling processes for mechanical alloying of nickel and copper alloys. During grinding, particle fracture occurs, which raises the temperature at the fracture tip to a few thousand degrees. As a result, mechanical fusion of one material over another occurs. In the case of diluting HEU with DU, the number of DU particles is much higher than the number of HEU particles. For this reason, it is expected that the DU particles will coat the surface of the HEU particles. This means that the dilution of HEU occurs at the particle level as well as in the bulk, blended product. This is significant when looking at potential processes based on slight density differences would be less effective at separating out HEU particles and any HEU that could be separated would already be significantly diluted.

PROCESS REQUIREMENTS

The HEU dilution process, as envisioned, consists of the following steps. The cans of HEU oxide are removed from the storage and placed in a glovebox. After opening, the material is sampled and measured and then combined with the DU material to reach the appropriate level of enrichment. The HEU oxide, DU oxide, and the grinding medium are then placed in a milling canister. After sealing the canister, it is placed in the mill for the grinding operation. After grinding, the canister is removed from the mill and the finished product is separated from the grinding medium and measured again for accountability purposes. The material is then ready for packaging for transport and the grinding media is recycled to the next milling canister

There are several technical requirements for the milling process that present significant technical challenges. Some of these requirements will be more difficult to successfully complete in a glove box environment than others.

- For criticality reasons, the canister is limited to 5” in diameter
- Blending must be done dry, again for criticality reasons
- The process must be designed for minimal handling to minimize material loss – the mass of HEU must be accounted for within fractions of a gram
- The process must be designed for acceptable personnel exposure
- The particles must be reduced to a size that is smaller than the feedstock (typically no greater than 1 – 2 microns). This is to eliminate physical separation based on possible color differences if unlike oxides are with one another.
- The grinding process must have enough energy to complete the size reduction in about 30 minutes to one hour. Lower throughput would impact the cost effectiveness of the process by requiring parallel installation of additional mills.
- The product must blend thoroughly, and in such a manner as to make separation of ^{235}U from the diluent extremely difficult.
- The process must operate efficiently in a glove box environment.
- When the grinding medium is removed from the process canister, measures must be available to reduce/eliminate the spread of material within the glove box.
- The process should be adaptable for robotic or mechanically assisted devices to load/unload process canisters and remove grinding medium from the LEU product.
- The mechanical reliability of the system should be capable of continuous service for extended operating periods (e.g., 4-6 months) and require minimal maintenance and downtime.

TECHNOLOGY SELECTION

Materials processing experts at the INEEL, and the Generic Mineral Technology Center for Comminution (GMTCC) at the University of Utah have evaluated available dry blending technologies to assess their adaptability and maturity. The GMTCC, which was established in 1982 by a grant from the U. S. Bureau of Mines, operates a series of specialized laboratories at the University of Utah including a characterization laboratory, size-separation laboratory, grinding laboratory, fragmentation laboratory, and a process evaluation/simulation laboratory. There are several technologies available for the grinding of oxide materials such as UO_3. The following technologies were evaluated against the unique requirements of the HEU blending process.

Ball Mill: The mill, for the purpose of HEU blending, would be cylindrical with lifter bars in the shell. HEU, DU, and ¼ inch steel balls as the grinding media would be placed in the mill. The mill would be lying on its shell surface over rollers that would spin the mill at approximately 105-rpm. The obvious drawback is that, with the mill diameter being so small, the impact forces of the media would be insufficient to grind the oxides down to the 1-5 microns needed.

Vibration Mill: The ball mill described above would be vibrated back and forth about an axis such that the balls rub against the powder and the shearing action would enhance the grinding. The major drawback is that the energy generated would require several days to grind the oxides sufficiently.

Attrition Mill: The attrition mill would solve the problem of the ball mills because it is a very high-energy process. In this process the canister would be filled with the HEU, DU, and 3-mm steel spheres as the grinding media. Unlike the conventional ball mills, the volume of grinding media would be very high -approaching 60% of the volume of the canister. This would add time and cost to the process.

Another disadvantage of the attrition mill in this application has to do with the way the mill is energized. The balls are agitated with shaft driven paddles at around 600 rpm. Packing of the powder will occur against the shell walls and the corners. In these regions the powder will not be well blended. Finally, mass accountability and personnel safety are potential issues. After the grinding is done, the lid must be opened and the shaft and paddle device removed. This has the potential for loss of material and the creation of hazardous dust and spills.

RM-2 Mill: The preferred technology evaluated, and selected for testing, is a patented technology called the RM-2 mill (Dual Drive Planetary Mill, U.S. patent # 6086242 July, 2000). This mill overcomes the disadvantages of the previous technologies by creating very high energy in a self-contained, sealed canister. The mill is based on the principle of a planetary ball mill operation where a very high gravitational field is developed by a gyration arm spinning at high speed with a ball mill that is independently rotating situated on the gyration arm. The RM-2 Concept mill uses novel mechanical parts to effect the centrifugal field and mill rotation. This novel design enables the mill to operate at very high centrifugal fields not possible with other mill technologies. Due to the energy generated by this centrifugal field, size reduction to ultra-fine sizes occurs very rapidly. The technology is well suited for small diameter mills because of this ability to generate high energy in the mill.

PROCESS TEST

The selected grinding technology was tested against two technical objectives. 1) a mixture of chemically similar oxide powders would be efficiently blended and ground into a fine, homogeneous product, and 2) it would be extremely difficult to separate the product to recover the simulated HEU through conventional chemical separation technology or by conventional mineral separation processes.

The RM-2 mill was set up in the GMTCC grinding laboratory and was easily modified for the simulated HEU dilution test. Because of university laboratory constraints, simulants for HEU and DU were used. Materials of different colors and different density were sought due to the possibility that it may be necessary to blend different uranium oxides e.g., U_3O_8 with UO_3, and also to aid in evaluating the blending thoroughness under optical microscope examination. While many candidate materials were available, titanium dioxide and titanium monoxide were selected for simulants of uranium oxides. These oxides of titanium will be referred to as dioxide and monoxide for brevity. The dioxide is pure white in color and monoxide is a dark greenish-brown. They exhibit a density of 4.26 gm/cc and 4.9 gm/cc respectively. The uranium oxide has a density of about 3.5 gm/cc.

The monoxide is much harder than the dioxide and both are much harder than UO_3 making the grinding test very conservative for the HEU dilution application of UO_3-HEU with UO_3-DU. Uranium ore has a grinding index of 14.6 and can fall anywhere between 10 and 20 depending on the source. The uranium oxide powders have about 10% of the strength of titanium oxides and it would be expected that the blended HEU and DU could be ground in about half the time required for the titanium oxides.

The test was conducted as follows:

The mill canister was filled with 20 gms of monoxide and 80 gms of dioxide. Alumina grinding media with a diameter of 0.6 – 1.0 mm was then added to a filling level of about 35%. The bulk volume of the media in the test was 350 cc and the mass was 700 gms. If steel media were used, the mass would have been increased to 1680 gms. The canister was then sealed and placed in the RM-2 mill. The centrifugal field of the gyration arm was set at 68G and the canister rotation speed set at 80% of critical speed. The sample was ground for exactly 75 minutes.

The canister was opened and the contents sieved on a 150-mesh screen to separate the powder from the alumina grinding media. The powder was then riffled to take four representative samples. One portion of the sample was used for size analysis and then all four samples were analyzed in an X-ray diffractometer.

TEST RESULTS

The size analysis of fresh samples was done with a Microtac SPA particle analyzer. This analyzer is based on the optical laser diffraction principle. The X-ray work was done on a Siemens X-ray diffraction instrument.

The average size of the feed was one micron with the maximum size of 75 microns. In the ground product the average was 0.5 microns with no particles larger than 1.69 microns. The feed and product size distributions are summarized in Table 1.

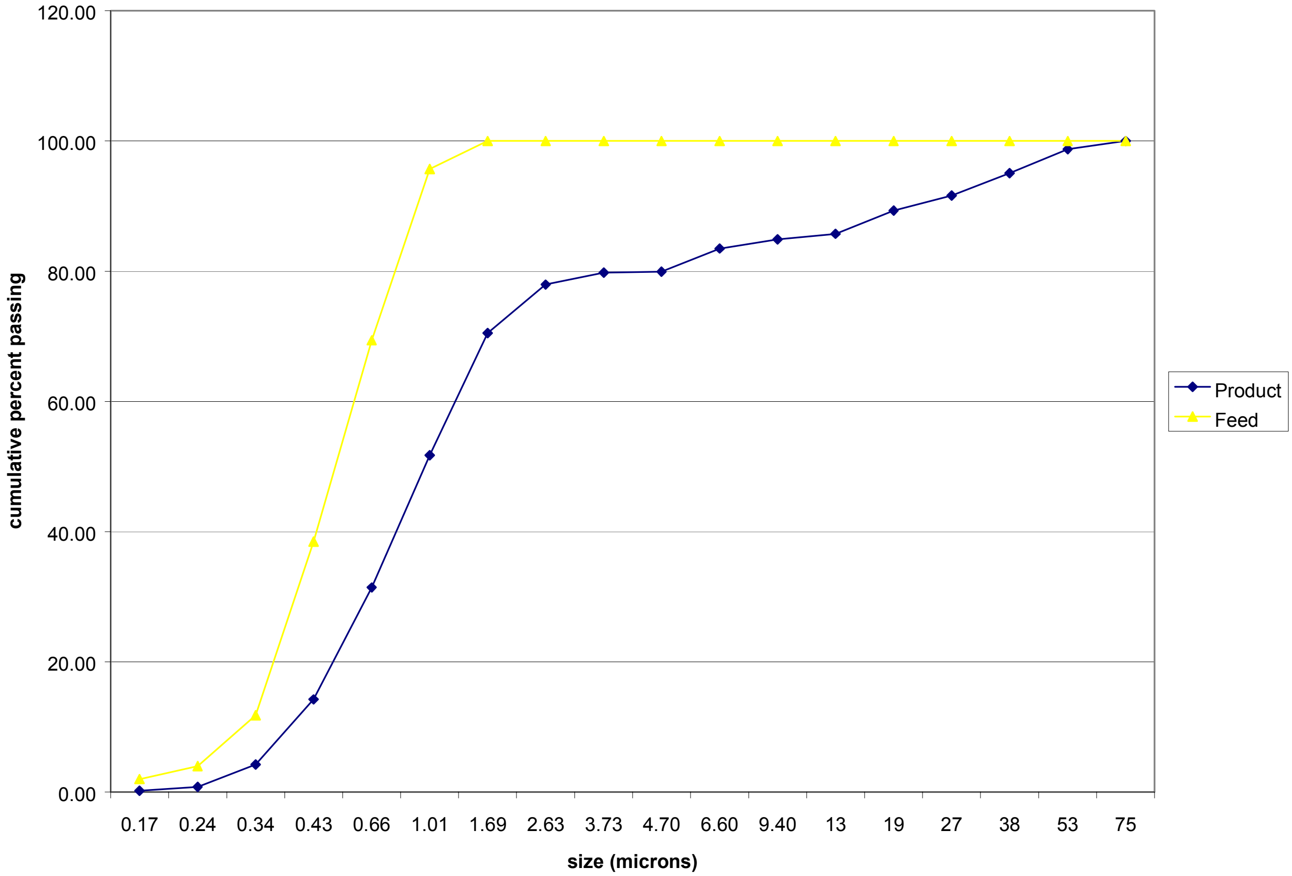
Table 1. Feed and Product Size Distributions

Size Microns	Percent Passing Feed (%)	Percent Passing 75-minute Product (%)
75	100	100
53	98.74	100
38	95.08	100
27	91.62	100
19	89.30	100
13	85.76	100
9.40	84.88	100
6.60	83.50	100
4.70	79.94	100
3.73	79.80	100
2.63	77.96	100
1.69	70.52	100
1.01	51.72	95.70
0.66	31.44	69.40
0.43	14.24	38.50
0.34	4.24	11.80
0.24	0.80	4.00
0.17	0.24	2.00

A large degree of size reduction was brought about in a short amount of time. At the same time, observation under the microscope indicates complete blending of the particles. The first objective of the test, efficiently blending the powders into a fine, homogeneous product, was a success. Figure 1 shows the feed and product size distribution.

For an analysis of the second objective, X-ray data was evaluated and a determination was made as to the difficulty of separating HEU and DU with conventional chemical or mineral separation processes, based on projections from the test results of. A subject matter expert with an outstanding technical understanding of uranium enrichment and extraction metallurgy reviewed the process and provided this evaluation. "The effectiveness of mixing oxides of uranium for the purposes of diluting enriched uranium (^{235}U) for safe shipment consists of two parts: 1) the ability to mix the enriched oxide to extensive dilution by your new grinding process; and 2) once mixed, the denial of any possibility of recovering enriched ^{235}U selectively by conventional chemical separation technology or by conventional mineral separation processes."

Figure 1. Feed and Ground Product Size Distribution



He agreed that, for the first part, the test had been successful in grinding and blending. For the second part he stated:

"X-ray results for the mixed oxides you have provided indicate extensive blending of the two titanium oxides to a degree of uniformity to support the use of this technique for the blending of oxides of uranium. To assure that the mixed oxides of uranium cannot be treated by some readily available mineral process technology, such as gravity separation or centrifuging, it is essential that the mixed oxide each be of the same chemical composition and density before the grind-blending treatment. Further, it is essential that in the ground product each oxide have the same size distribution. The latter is important so that separation techniques based on size or on size and density cannot be used to separate the isotope selectively."

"To address the second issue, I assume the mixed $^{235}U/^{238}U$ oxides meet the above conditions; namely thorough, uniform blending and oxides of identical composition, density and size distribution in the final product. If these conditions are met, I concur with you that separation of the isotope by physical means will not be possible. Similarly we can conclude, because of the identical chemical properties of each of the mixed oxides, that chemical separations by conventional dissolution, extraction and recovery using aqueous processes as well as high temperature processes such as molten phase separations will be ineffective as a means to separate the isotope."

CONCLUSIONS

The conclusion of the test of the RM-2 technology and the subsequent analysis of the powders is that the grinding/blending requirements were met and that the product would have very high proliferation resistance. Feasibility testing with surrogate materials (titanium monoxide blended with titanium dioxide) has produced excellent mixing results. Due to the centrifugal forces, size reduction to sub-micron particles occurs in a matter of an hour. The blending is irreversible and has received a favorable security/proliferation review from Los Alamos National Laboratory. When the "off-spec" HEU is dry blended to less than 20% ^{235}U enrichment, the radiation fields from the storage containers will be reduced, the uranium will no longer require safeguards and the potential for shipping to an "off-spec" aqueous blending site will be significantly improved. This same technology could also be used to dilute waste HEU oxide to less than 0.9% ^{235}U for disposal should that disposition path be selected.

KEY ISSUES TO BE ADDRESSED

There are several key issues to be addressed in the next phase of the project. This phase would scale up the mill and run extensive tests on actual U oxides at the University of Utah facilities with natural and depleted uranium feed materials (UO_3) to:

- Evaluate milling and blending equipment with uranium oxide materials to determine blending times, throughput rates, and potential for cross contamination of milling media and U, and can design to preclude any "dead spots".

- Evaluate the effectiveness of this equipment for mixing different oxides (e.g., UO_2, U_3O_8, UO_3)

- Evaluate material handling and contamination control issues as related to this specific equipment and the related process steps e.g., adding depleted uranium oxide and enriched uranium oxide to the mixing canisters, sealing techniques for the storage packages, taking accountability measurements, etc.

- Optimize the equipment design and procedures against the site-specific functional and operational requirements for INEEL HEU oxides.

Another key issue is complex-wide acceptance of this isotopic dilution technology. DOE has initiated numerous activities to focus on identifying material management strategies that can integrate resources to reduce operating costs and also accelerate the retirement of facilities and the dispositioning of excess fissile materials e.g., *EM Integration/2006 Plan*, *Processing Needs Assessment* study, *Integrated Nuclear Materials Management Plan* and others. This technology could have a significant impact in this area but it needs to be more fully developed and proven. Planning strategies have not fully evaluated this technology to achieve isotopic dilution, however some plans have included this technology is disposition paths.

If this technology is proven to be adaptable to dispositioning excess fissile materials, then the dispositioning site would have a non-aqueous option that could be significantly less costly than aqueous and/or pyrochemical technologies. Dilution to less than 20% would also reduce storage costs until such time as the final dispositioning process was implemented. Furthermore, a dry process can be sized to meet throughput rates, is expected to require less operating space, and should provide unique schedule flexibility because dispositioning would be de-coupled from the retirement of existing aqueous processing facilities. The compactness of the process could also lend itself to being a portable system that could be used across the DOE complex to disposition small inventories of materials in a cost-effective manner.

The DOE is planning to further develop this technology or another dry blending technology. A call for proposals has been issued under the auspices of the Nuclear Materials Focus Area for Applied Research. Funding is anticipated to conduct additional research using NU and DU oxides. Should the technology prove effective, the equipment may to be transferred to the INEEL for demonstration and deployment using HEU and DU oxides.