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Title: Recovery of Pu-238 by Molten Salt Oxidation Processing of Pu-238 Contaminated Combustibles (Part II)

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Recovery of $^{238}PuO_2$ By Molten Salt Oxidation Processing Of $^{238}PuO_2$ Contaminated Combustibles (Part II)

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Abstract. Pu-238 heat sources are used to fuel radioisotope thermoelectric generators (RTG) used in space missions. The demand for this fuel is increasing, yet there are currently no domestic sources of this material. Much of the fuel is material reprocessed from other sources. One rich source of Pu-238 residual material is that from contaminated combustible materials, such as cheesecloth, ion exchange resins and plastics. From both waste minimization and production efficiency standpoints, the best solution is to recover this material. One way to accomplish separation of the organic component from these residues is a flameless oxidation process using molten salt as the matrix for the breakdown of the organic to carbon dioxide and water. The plutonium is retained in the salt, and can be recovered by dissolution of the carbonate salt in an aqueous solution, leaving the insoluble oxide behind. Further aqueous scrap recovery processing is used to purify the plutonium oxide. Recovery of the plutonium from contaminated combustibles achieves two important goals. First, it increases the inventory of Pu-238 available for heat source fabrication. Second, it is a significant waste minimization process. Because of its thermal activity (0.567 W per gram), combustibles must be packaged for disposition with much lower amounts of Pu-238 per drum than other waste types. Specifically, cheesecloth residues in the form of pyrolyzed ash (for stabilization) are being stored for eventual recovery of the plutonium.

^{238}Pu Science and Engineering Bench-Scale Molten Salt Oxidation Process

STAIF 2005

Lyndsay Remerowski
Los Alamos National Laboratory
Nuclear Materials Technology Division
Pu-238 Science and Engineering Group

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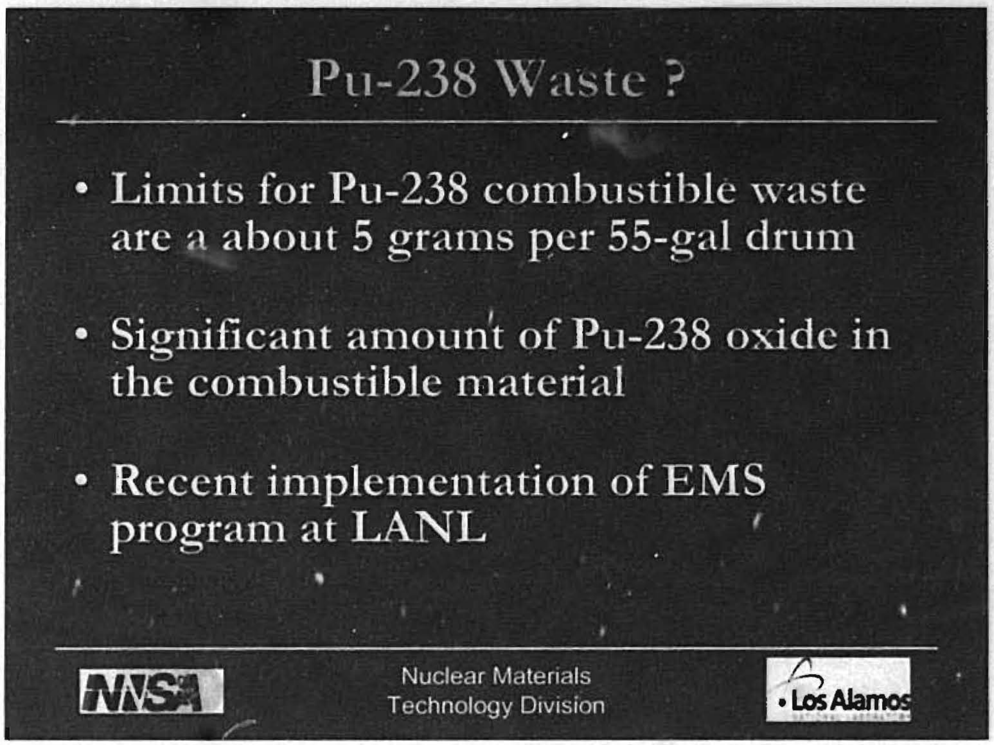
Voyager, Galileo, Cassini, Pluto

Need breeder reactor. Used to be at SRS. May bring up again?

We don't know what. Rule is that no Russian material be used for defense purposes.

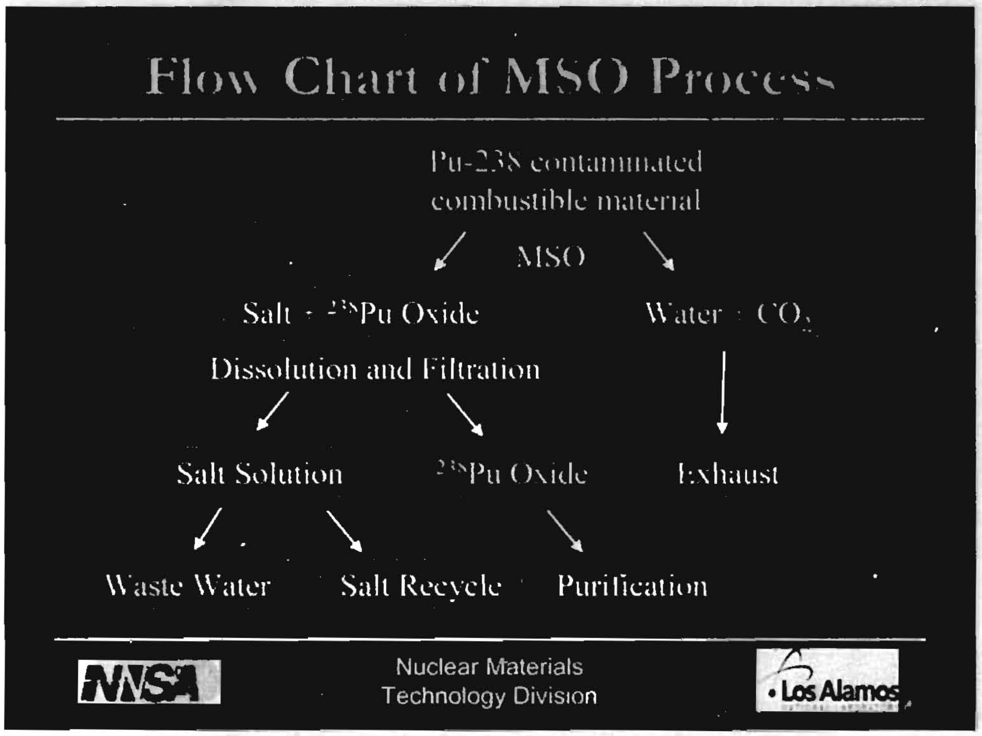


Environmental Management System required by all DOE facilities by 2005. Requires continual improvement in environmental program

In the 70's molten salt technology was developed by Rockwell for DOE. Application to mixed rad waste. Incineration was easier.

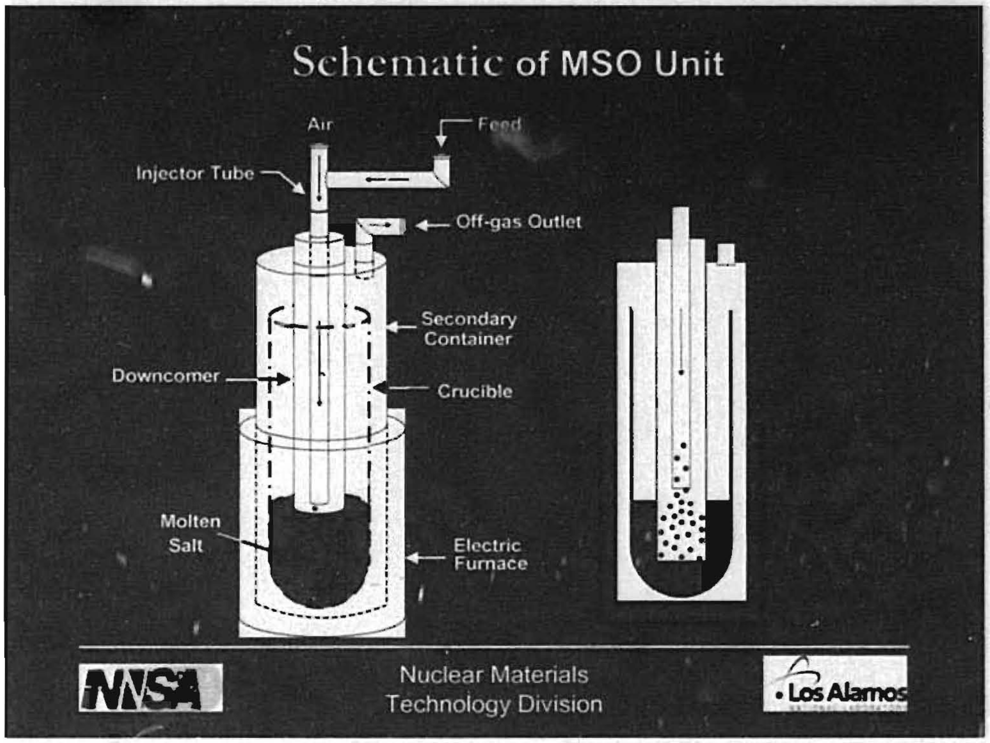
Incineration no longer option, molten salt was revived in the 90's because it provided a **flameless alternative to incineration. The salt provides a hot matrix to drive the complete oxidation of hydrocarbon materials.**

The plutonium remains in the salt. This is key to our application as we want to recover the oxide from the salt. This application not been explored previously.



After treatment by MSO the Pu is reclaimed as shown.

The Pu oxide is insoluble in water, so can be easily separated from the salt by dissolution in water and subsequent filtration. The oxide is sent to aqueous scrap recovery for purification. The salt can be reclaimed from the solution for reuse in the unit, or the entire solution disposed of as liquid waste.



Here is the basic unit.

Here is the molten salt bed. It sits in a crucible of either ceramic or Inconel 600. We are using ceramic, which has its advantages and disadvantages as we shall see. We have the ceramic crucible sitting inside another thin-walled container made of Inconel 600. Finally there is the secondary containment, also of Inconel 600.

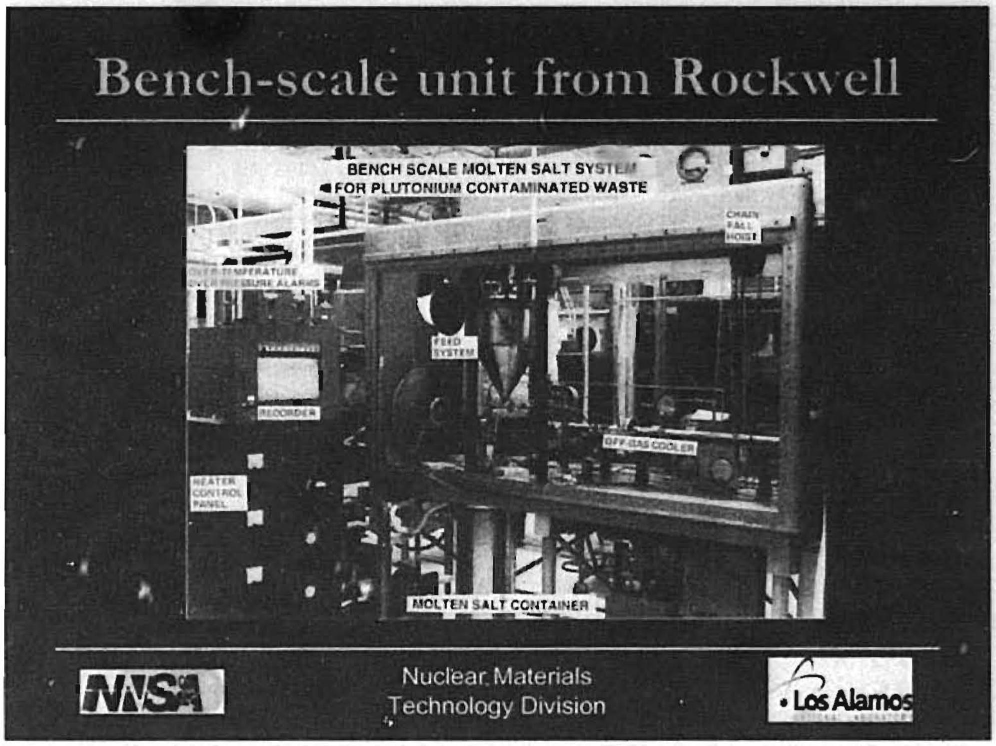
Note the furnace is not the full height of the unit. Typically the unit is the same size as the furnace. Ours is different due to the available space in the glove box.

The air and feed is mixed and enters the unit via the injector or feed tube.

In the unit, the tube is inside another called the downcomer. The feed tube sits above the salt so it does not become clogged by corrosion and/or oxidation occurring at the tube/salt interface. The downcomer annulus also provides a cooling layer of air to help prevent early oxidation. It is to our advantage from this standpoint that our unit sits partially outside the furnace.

The air pressure pushes all salt outside the downcomer and the air/feed is forced out the downcomer. The end of the downcomer is near the salt bed bottom to maximize residence time.

Downcomer is sheath to protect feed/air tube. The feed/air tube sits above the salt to avoid corrosion. Downcomer sits near the bottom of the salt to maximize residence time and protect feed/air tube. Feed/air is pushed down the introduction is through an eductor

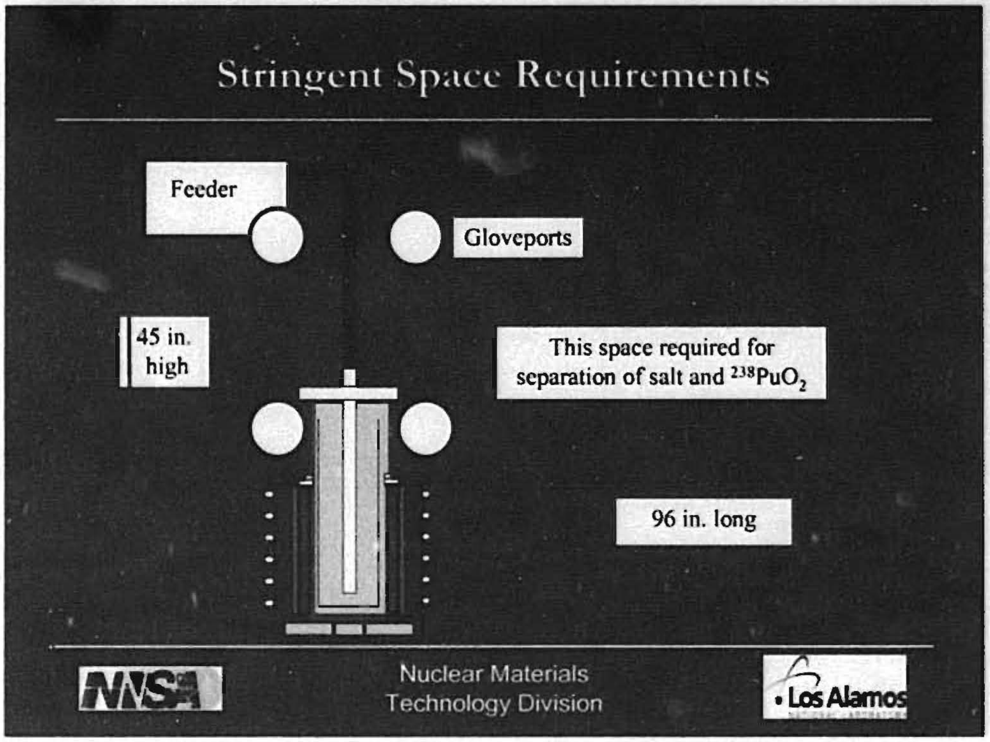


We are certainly not starting from zero in the construction of such a unit. Here is a glovebox unit built by Rockwell in the mid-70's. 3g/min waste with small amounts of Pu (0.1%-0.01%)

MSO technology was revived in the 90's in areas of the DOE complex. Today there are working units at Hanford, Indian Head Navel Surface Warfare Center.

Significant differences between what went before and ours. They built their box around the unit. We.....

1. Build into existing space. Height/space/safety issue
2. Recover material. Materials and safety issue
3. Feed type. Feed system to handle the light fluffy ash. This ash is the product of a pyrolysis procedure applied to Pu-238 contaminated cheesecloth. The result is a light, dusty material with tiny fibers left from the cheesecloth structure.

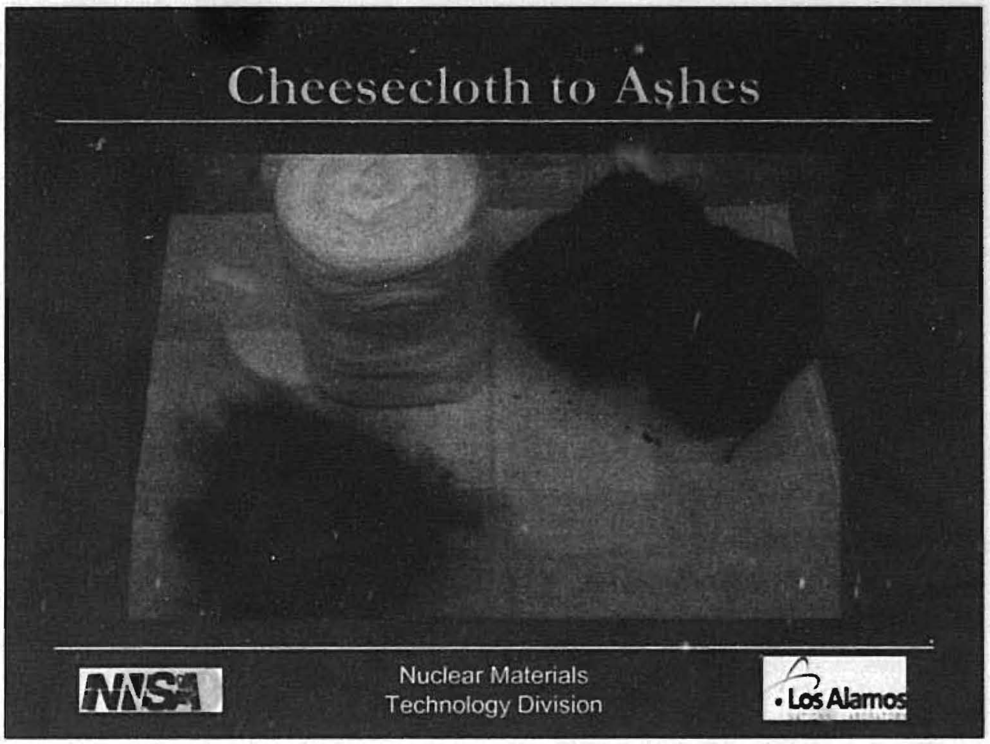


Glovebox was not fit to have any operation remotely similar to this one. Tidbit, the lower ports are unnaturally far apart. Top ones are not in alignment. The furnace is not spaced in exactly between the glove ports.

Glove ports on three sides but only one set is able to provide reach to work with the unit in the furnace. **Even at this height taking the crucible out of the unit will be a two-person job.**

See limit to **height unit, and furnace size**. Height is important to MSO because of the frothing and splash from bubbling air through the salt. Pretty vigorous. Salt entrainment and consequently clogging of exhaust line results.

There is **not much room for a feeder**. So small needed. Sources like pharmaceutical industry.



Pix of cheesecloth and ash

Dusty and light

Pyrolysis is way to stabilize material, remove combustible and size reduce.

Challenge to feed system, cannot gravity feed or mechanically feed easily

Choose eductor as method to introduce feed into

Pix of cheesecloth and ash

Dusty and light

Pyrolysis is way to stabilize material, remove combustible and size reduce.

Challenge to feed system, cannot gravity feed or mechanically feed easily

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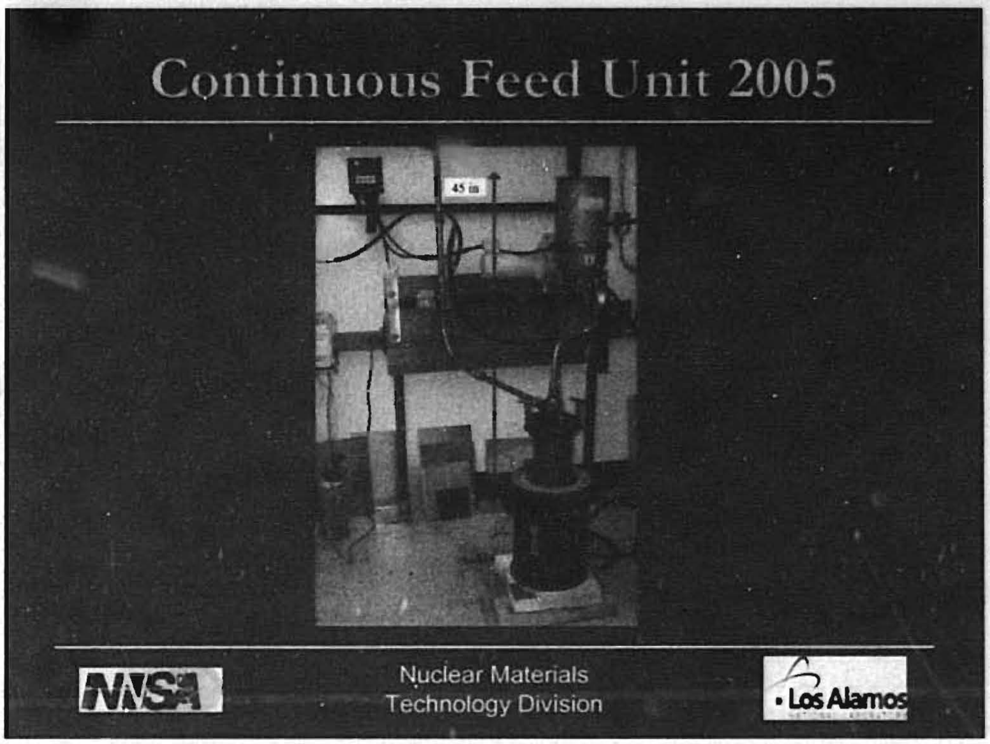
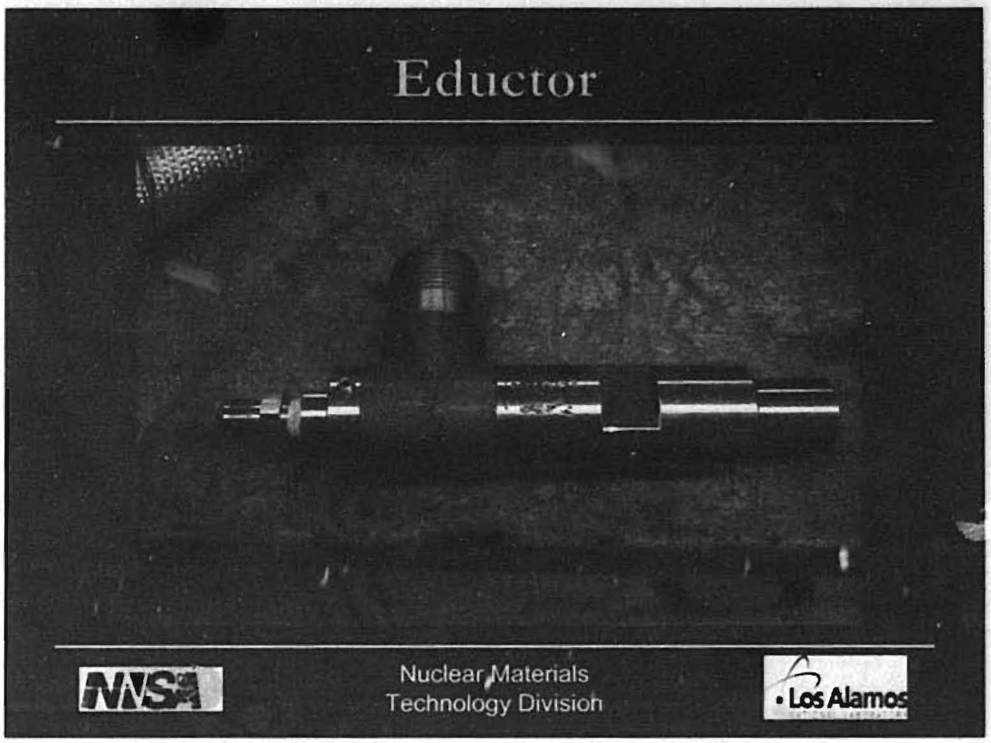


Screwfeeder – Difficulty finding a mechanical feed system for ash.And still have the size consideration. Experiment with this small screwfeeder. Result is bridging.

There are two directions to go if that is the case. Additive to make feed friendlier. Also, better oxidation. Or find mechanical system that works. The small screwfeeder didn't work

A lot of added height from the 90 bend we need between feeder and unit entry. Due to use of eductor. (Next slide)



No gravity system will work with ash. Venturi nozzle to create suction and acceleration of feed into the unit.

It has some weaknesses since most are used under high pressure and volume air relative to our situation. Suction is not strong

Too much air will create salt carryover. That is why the unit is as tall as it is to begin with. And we have already shortened the unit as much as possible to accommodate our GB space.

The ash is also irrecgular and sticks in the narrowed opening. Especially at the lowered pressure and air flow.

Earliest attempts were to change feed. Ground up plastic feed very well. So...

Melt plastic beads and add ash

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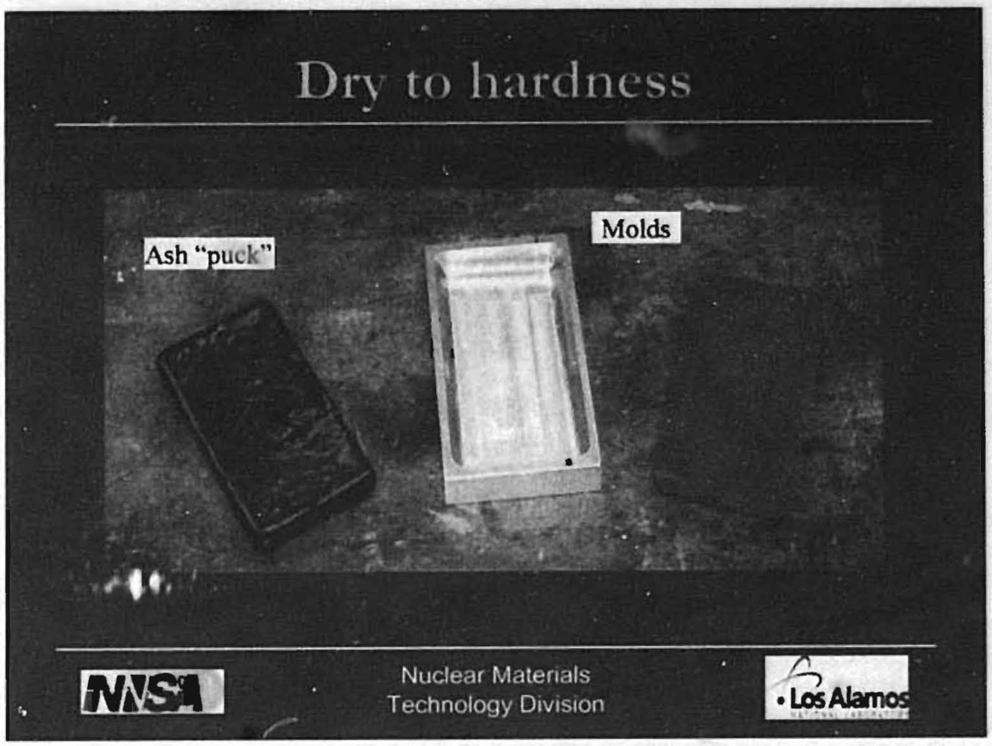
Dry to hardness
Ash "puck"
Molds
NNSA
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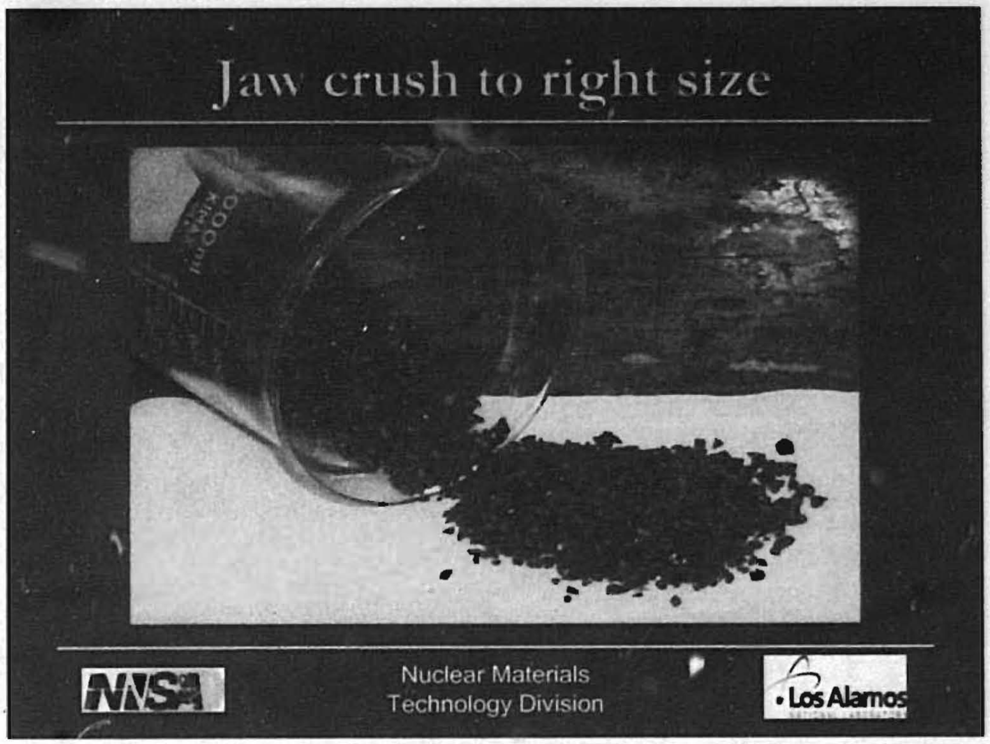
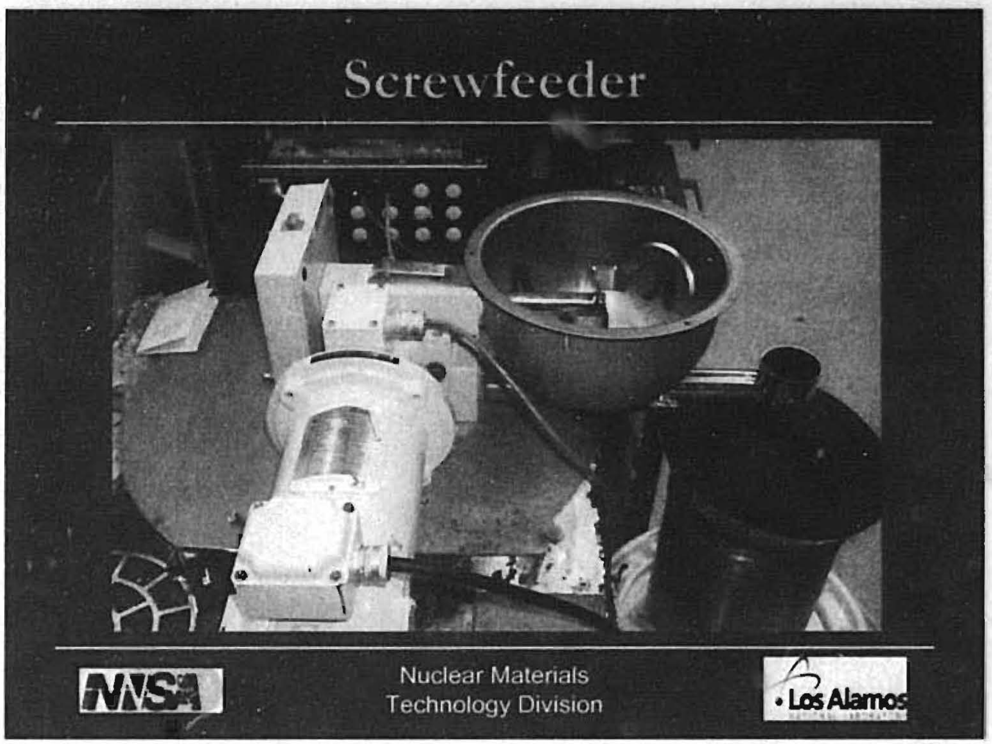


Problems. Operator exposure. Only 10% ash "fits" in to plastic, so throughput would be decreased. How much depends on the material.

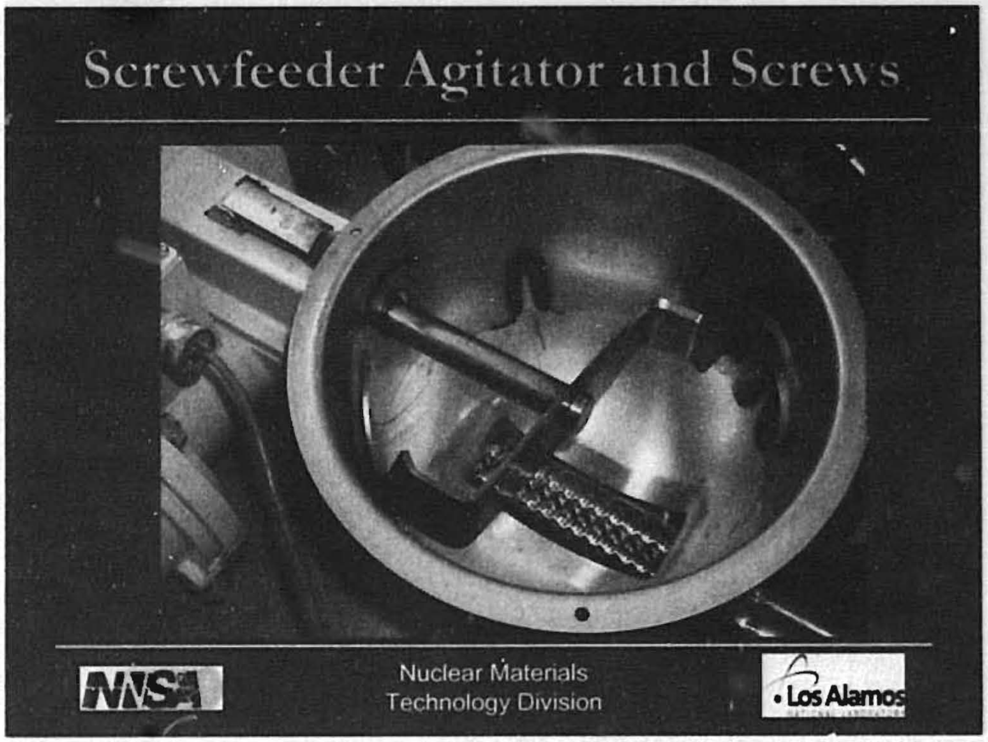
Efforts still being applied in this direction.



Another problem was mechanical feeding. We knew a screwfeeder would work well, but needed to find one that was small enough to fit in the box and had agitation to push the light feed into the screws. We found a small one early on, but feed bridged, so knew we needed some agitation.

Found KTron, 35 lb, 18 in long, with a very good agitator. The only fly in the ointment is that the motor is perpendicular to the feeder. It fits more awkwardly in the box that way. We tested a Brabender that had one parallel, but it had other flaws.

Our machinist and technicians just love to innovate and sometimes the ash can be clumpy, so....


Screwfeeder Agitator and Screws
NNSA
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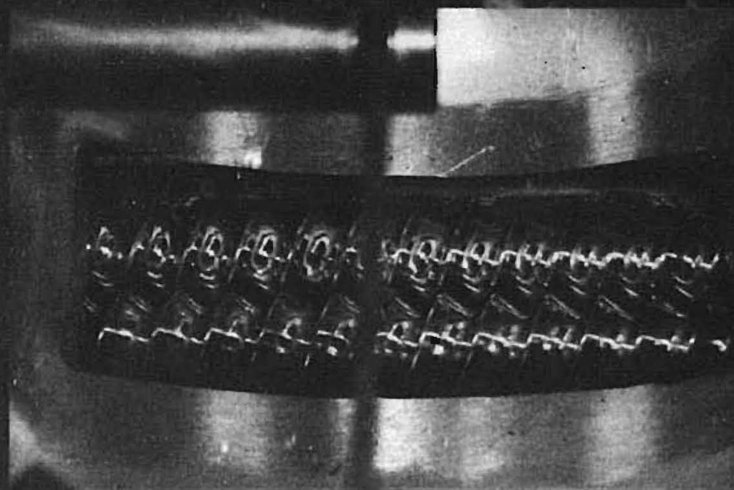
Double Screws



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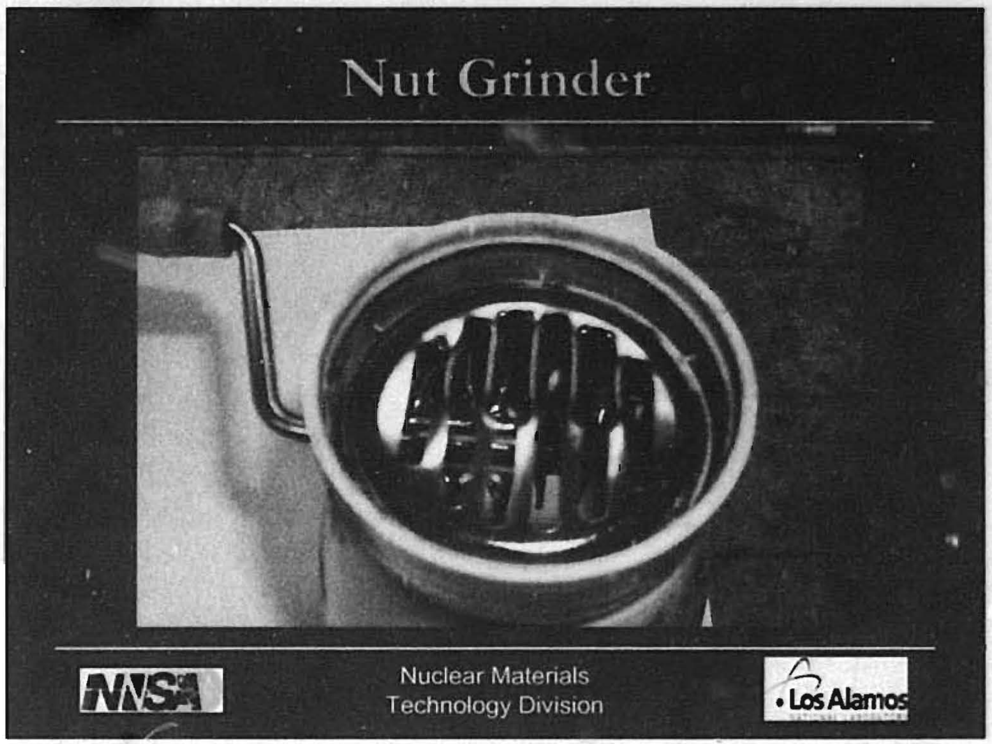
Nut Grinder
NNSA
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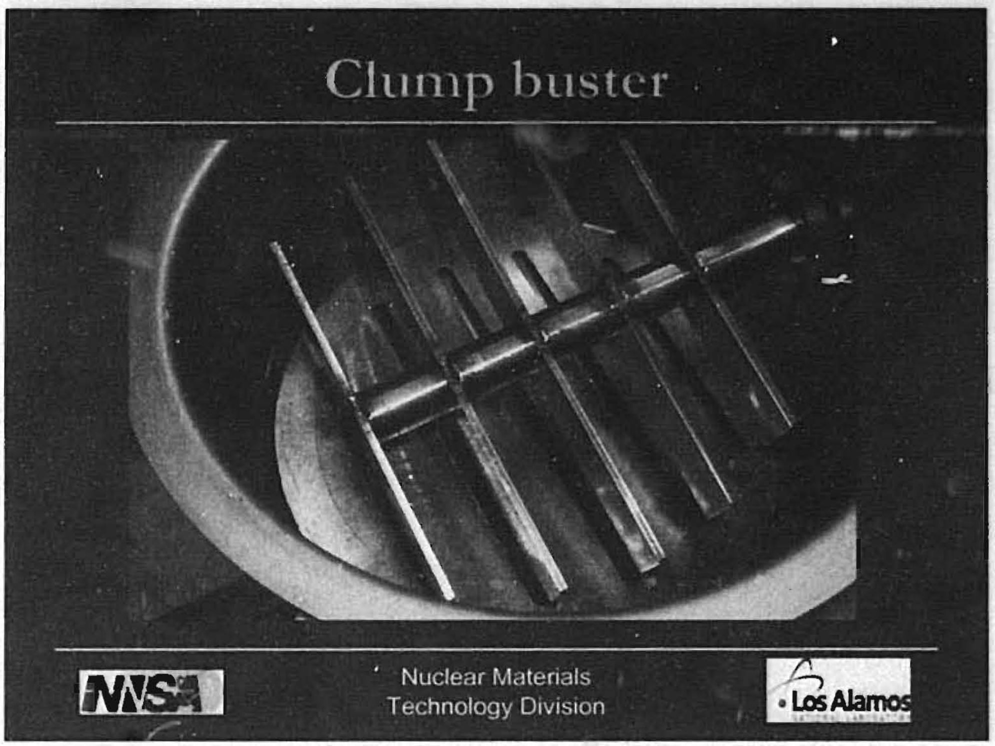
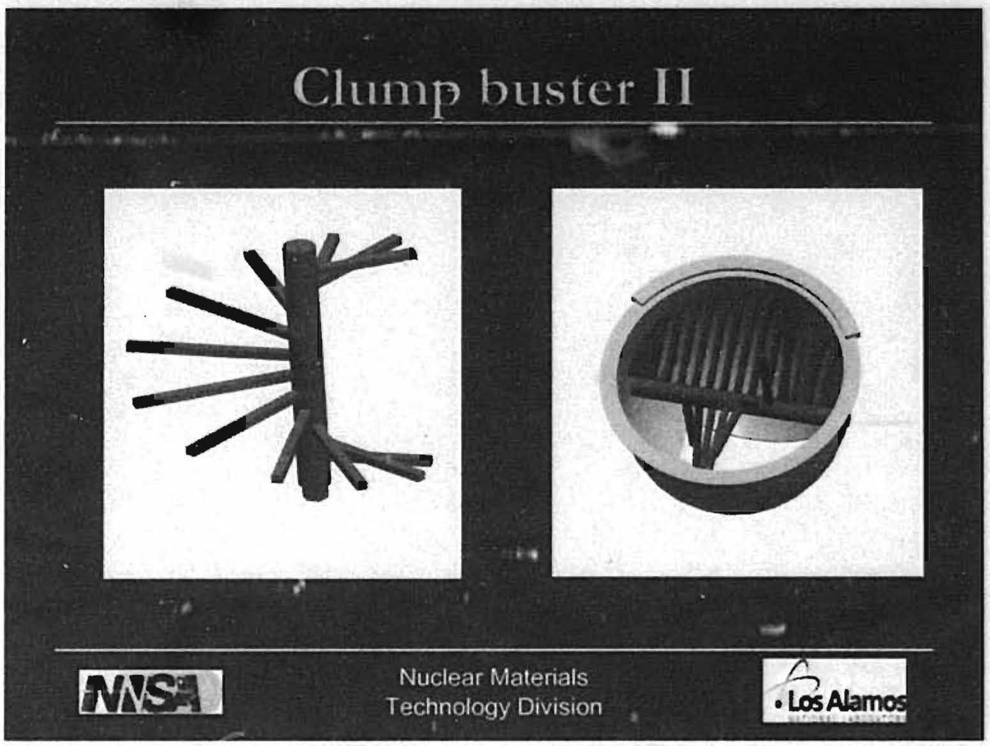


Design based on a nut grinder that worked pretty well

Fashioned the original clump buster, and of course during the shut-down, having a lot of time on their hands, our technician Joe Romero designed another one.


Clump buster II
Nuclear Materials
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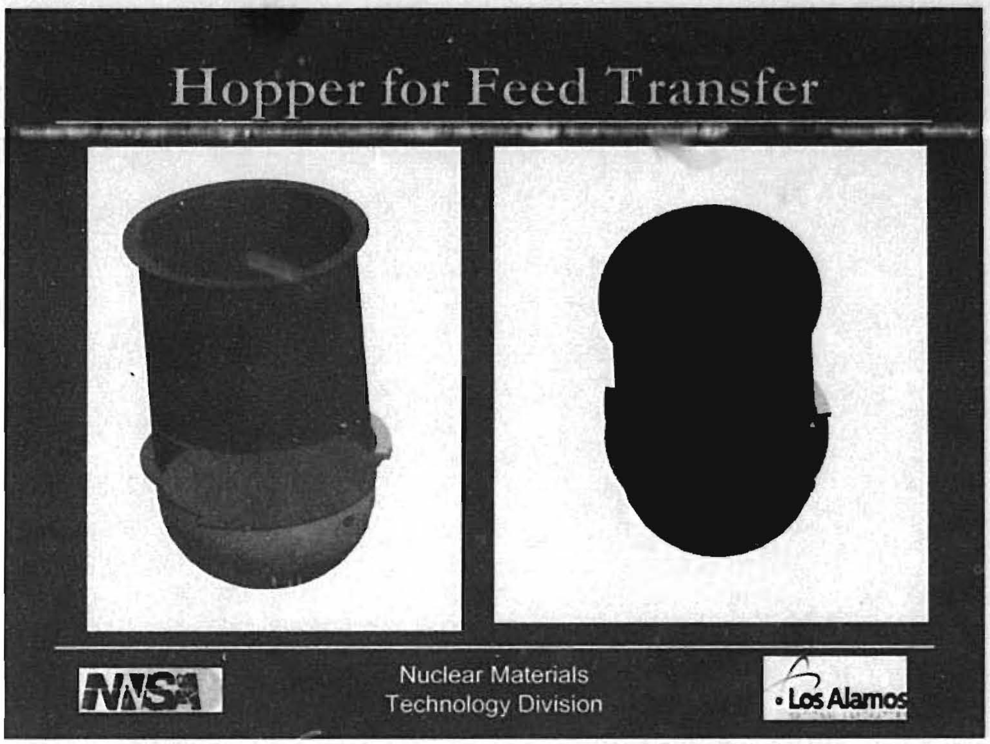
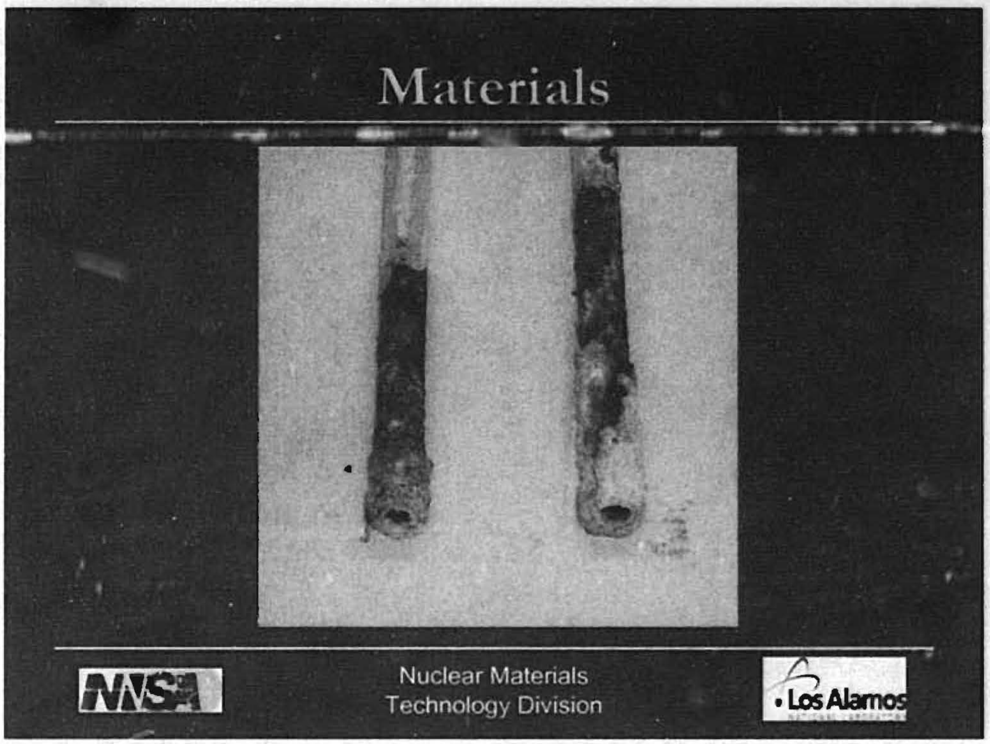


Also want to increase size of hopper somewhat with more funnel like hopper



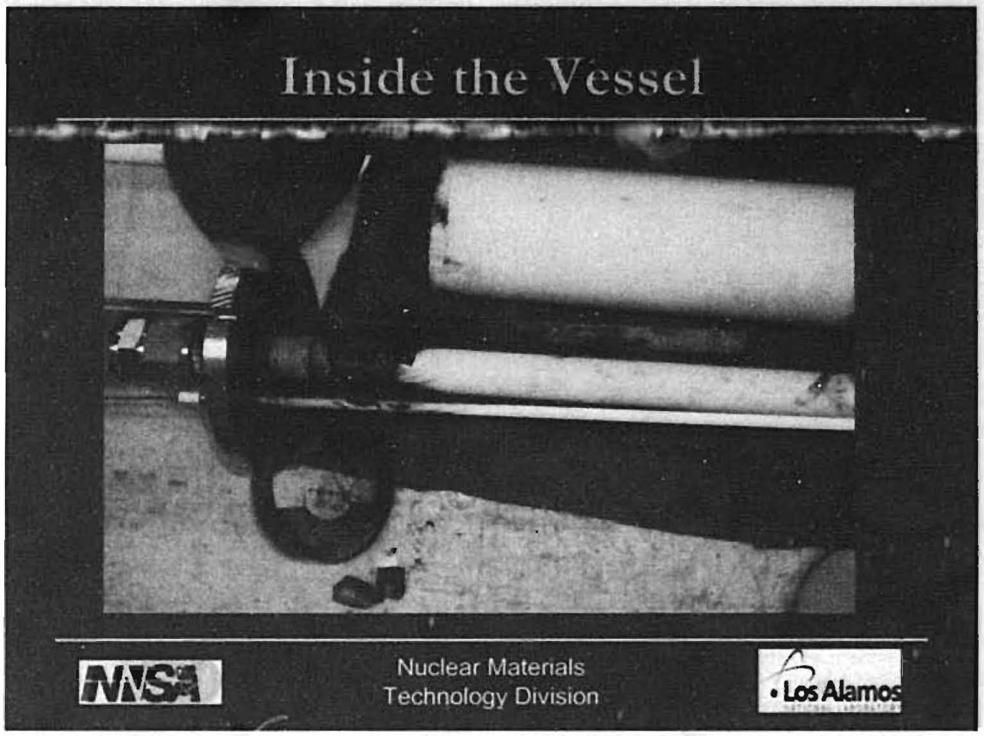
Very alkaline, oxidizing, high temperature is a recipe for corrosion

Studies showed Inconel 600 to be most corrosion resistant of metal materials. (These are stainless)

Even Inconel 600 corrodes over time leaving metal oxides in the salt and chromate in salt solution.

One reason we chose to go for ceramics. The oxides are most corrosion resistant. Greater than metal.

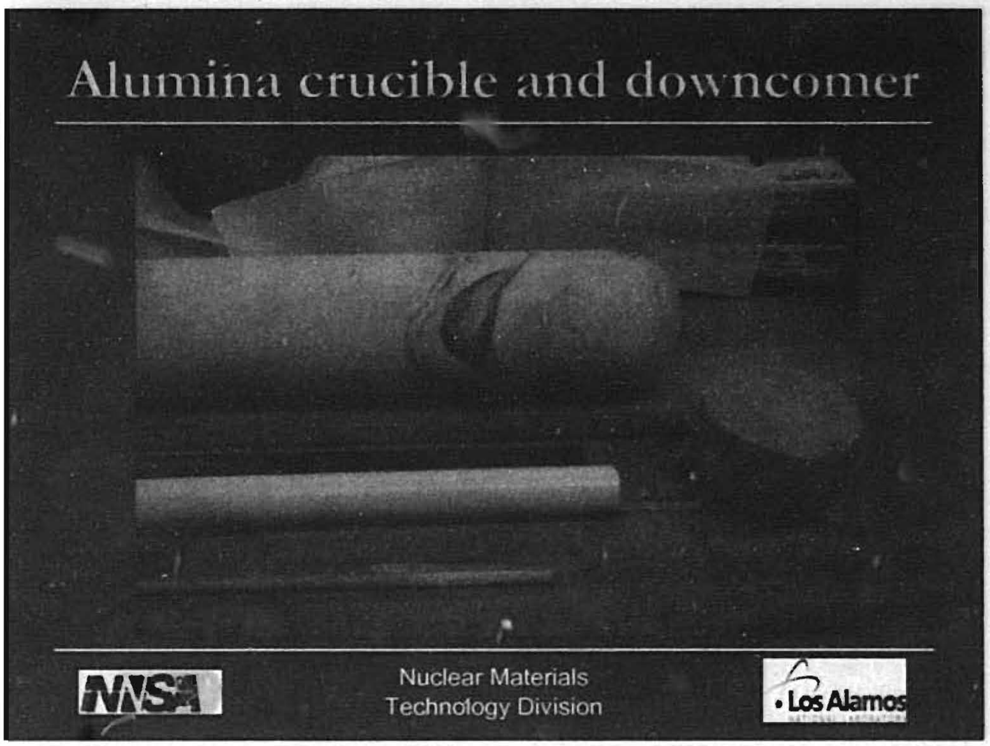
But we know it has a problem



Oxide ceramics have limited thermal shock resistance. And they are fragile.

In the continuous feed unit we have the downcomer over the feed tube. Good view because it is broken. Problem with ceramic. Decision to go with the Inconel 600 downcomer made. Trade corrosion products in the salt for added safety and ease.

1. Ceramic cannot survive being frozen in the salt. So need to lift it out while unit is hot.
2. Break easily. Need to manipulate it more.

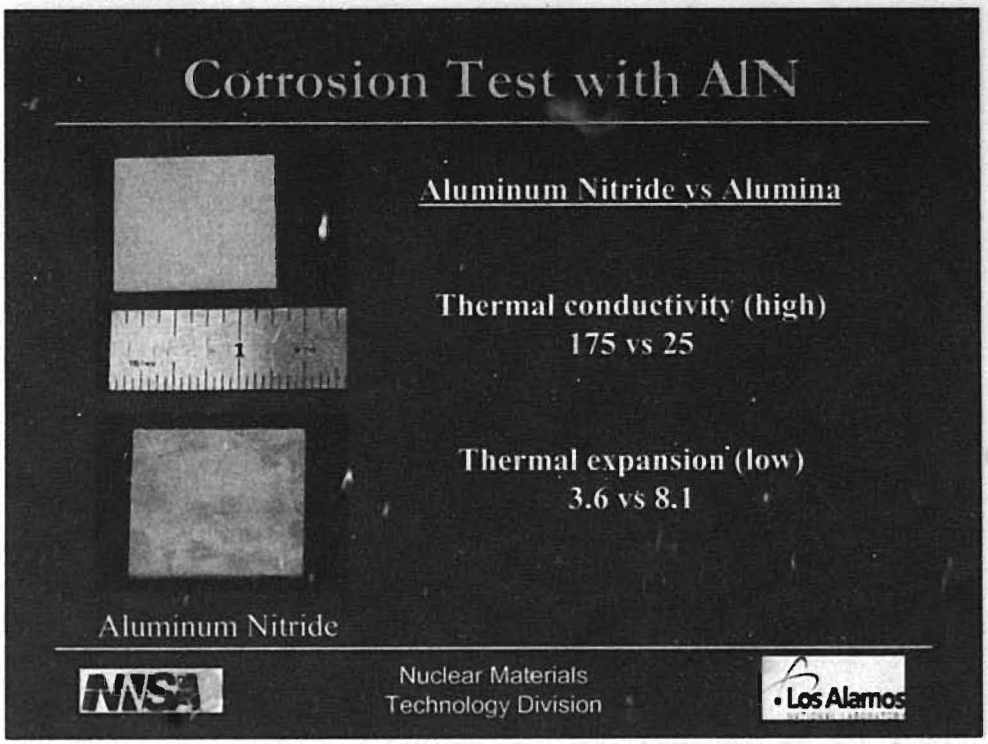


Secondly, the salt does not stick to ceramic. Look at salt plug. When metal is used the salt turns to cement. There is no way to separate from the crucible. Others use a vacuum suction system that takes the still molten salt from the crucible into another containment. The salt freezes instantly, and actually comes loose. Doing that in glovebox is not feasible. It has been done, but if we can avoid it we will not do it.

Alumina has been used by earlier workers. Abandoned because of thermal shock sensitivity. In our case, it is not so bad because we are using smaller crucibles. Configuration is very important. Alumina works OK. Gotten 13 runs out of smaller crucibles.

Tested known thermal shock resistant ceramics. SiAlon melted. Anything with silicon was vulnerable. Mullite actually came out the best. Other type was a titania-alumina composites. Melted or extremely corrodible.

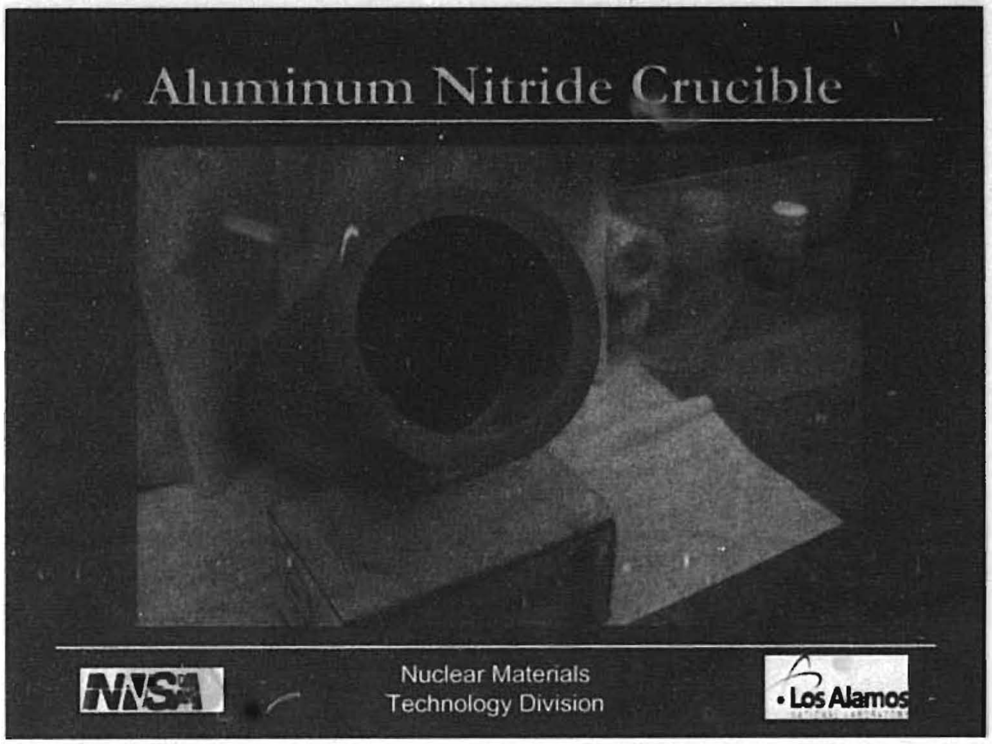
Aluminum nitride was extremely corrosion resistant. Seemed to form an oxide layer. Test was five weeks at 900C or above.



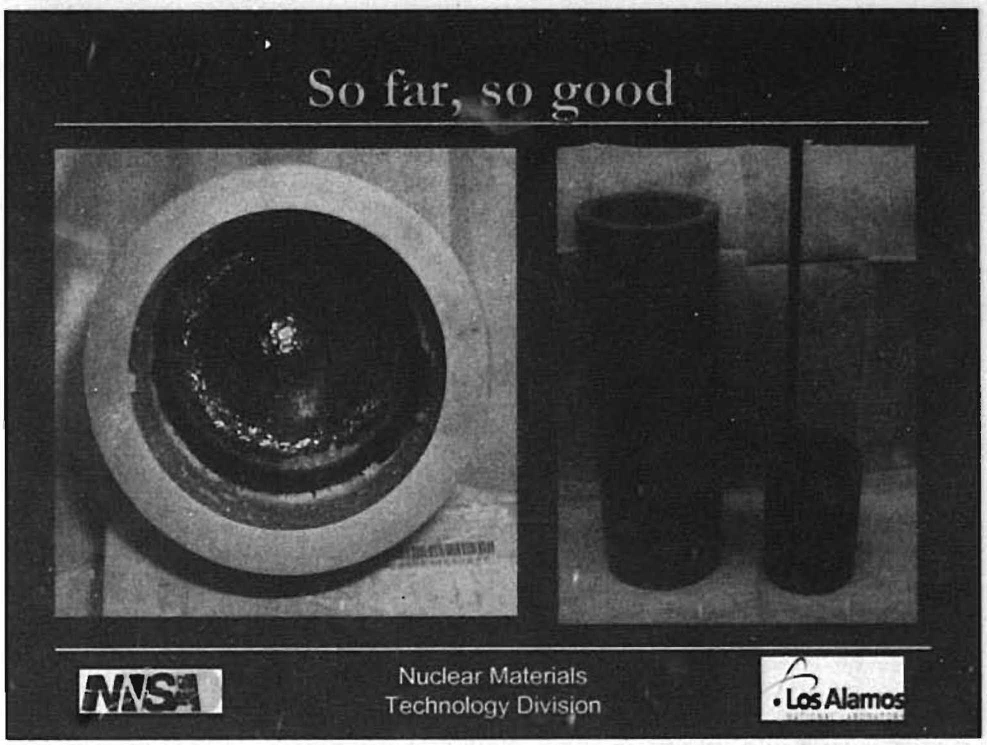
Alumina is the standard. Used because of corrosion resistance, inexpensive.

Think get an alumina layer

Also want to test titanium-aluminum carbide/oxide

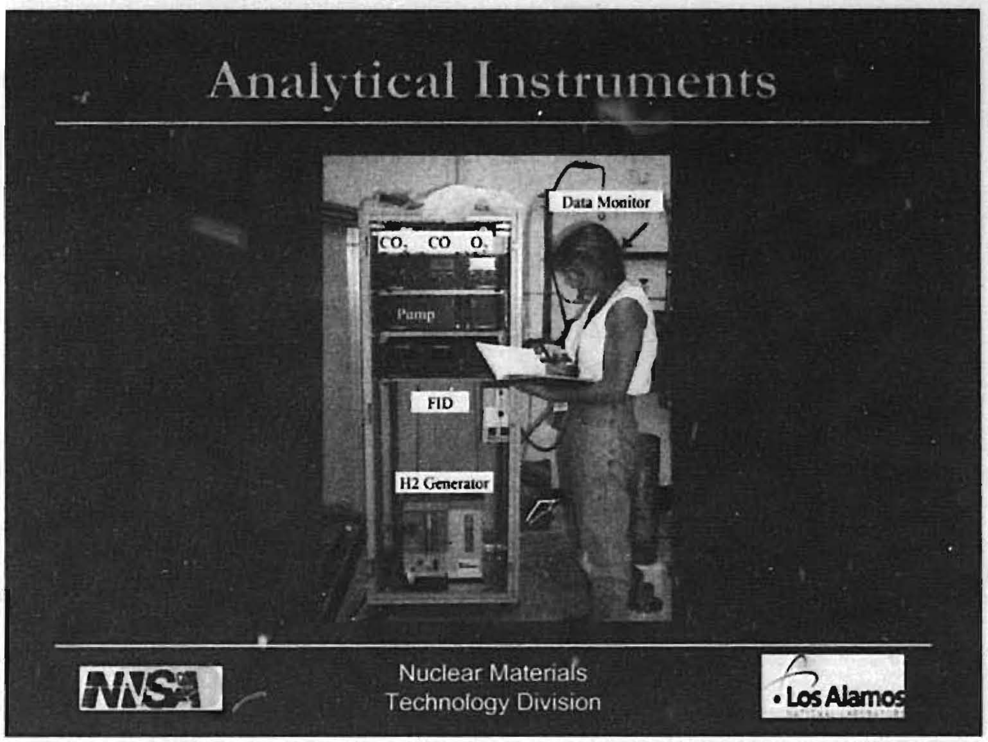


Problem in fabrication. One vendor took it on. Three pieces cemented together. Had to make it thick so it wouldn't crack with such a large size. So it is heavy

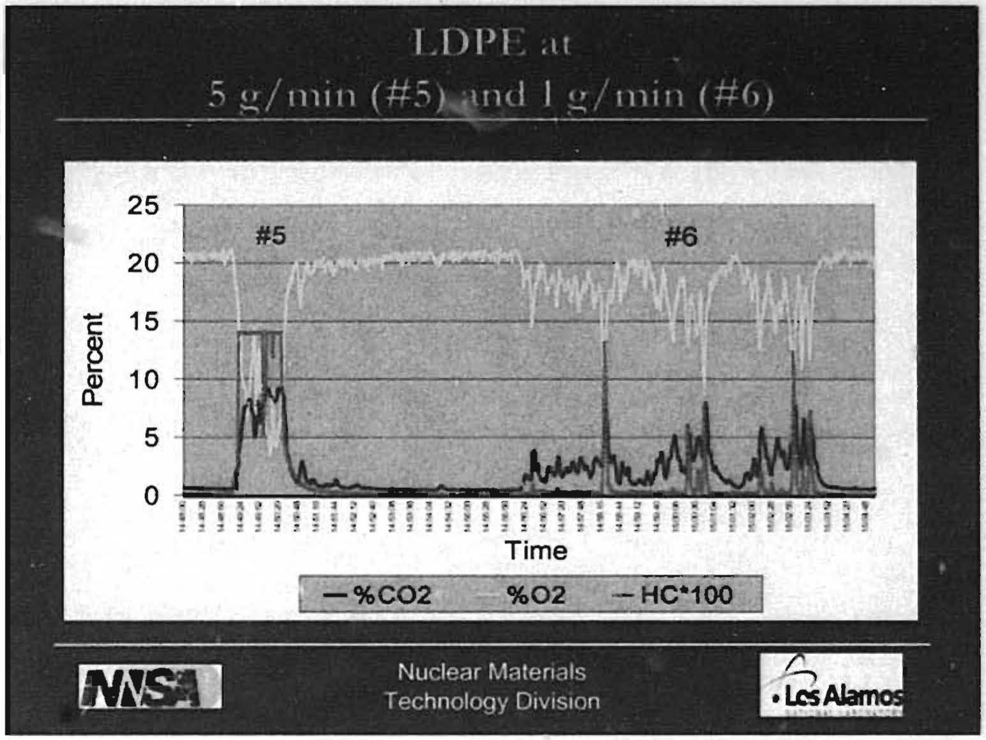


Trying to test it by ramping it each day and bubbling air through it for a few hours. Want to see how well it stands up to repeated thermal changes. Done four times so far.

Bonus: Salt does not wet. We were able to easily slip the salt plug out of the crucible using the metal bar as a grab handle, like a popsicle stick.



Started work in 2002 with continuous feed unit. No screwfeeder, no data monitor, just humans.



Got the thing to work.

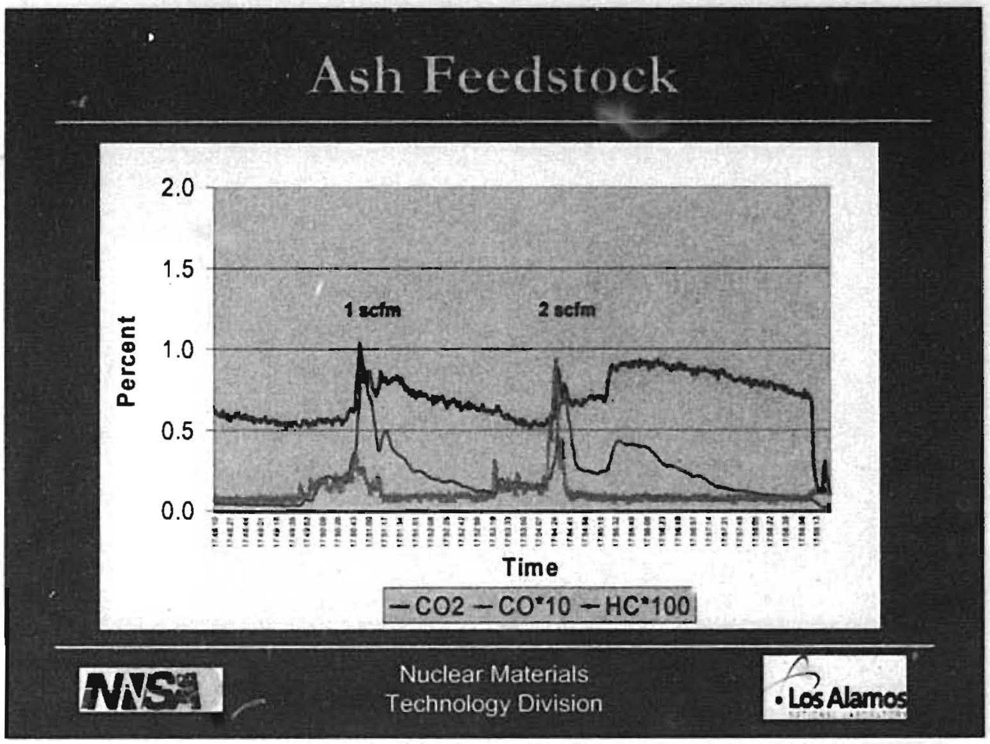
See here off-gases. Shown is O2, CO2, HC (scaled differently).

CO2:CO usually 10:1.

HC in 100-1000 ppm range. Vary with material. We are using Low Density......

Note spikiness, due to hand feeding.

Not total efficiency at 5 g/min, but a much better feed rate. Still working on the chemistry.



Ash is a much harder feed stock

1 g/min compare CO2, CO, HC

Two-pronged Approach

- Install batch mode unit in Pu Facility
  - ✓ Small unit, authorized for batch mode
  - ✓ Experience with glovebox and PuO_2
- Continue to develop continuous mode unit
  - ✓ Materials testing for crucible
  - ✓ Scrwefeeder improvement

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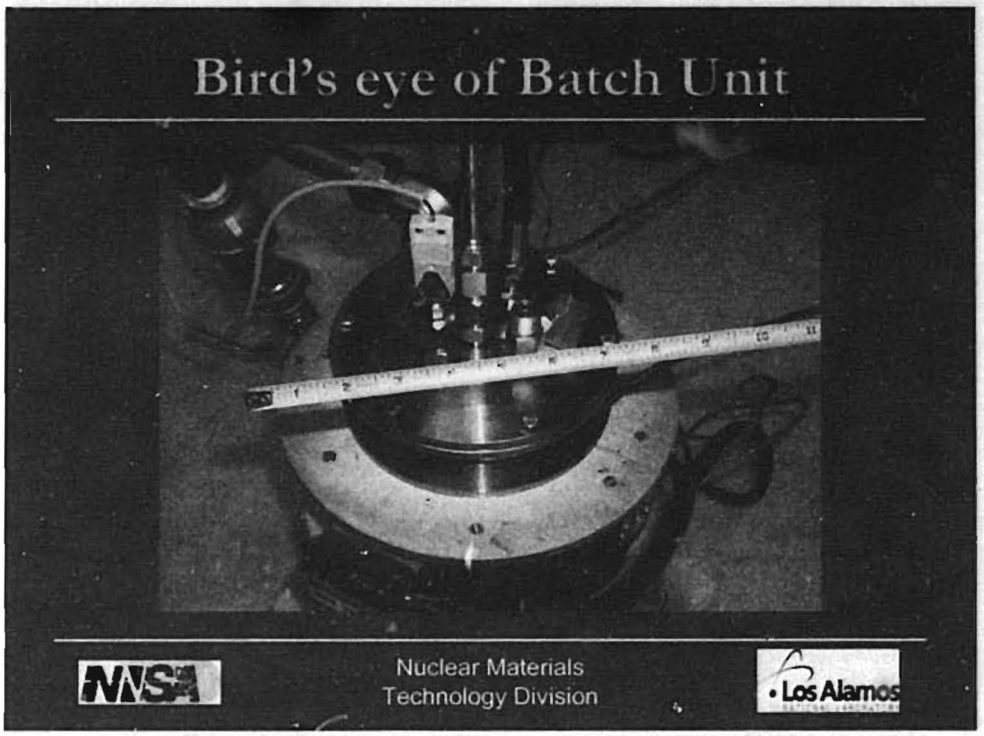
Hadn't solved the materials and screwfeeder problem, so went to the two-pronged approach.

The batch mode is a **less complex** operation and **similar to another pyrochemical process** previously performed in that space, so the batch mode MSO is **allowed under existing safety envelope** established then.

Wanted to test how Pu-238 would behave. Would it fall to bottom as predicted? Could it be removed?

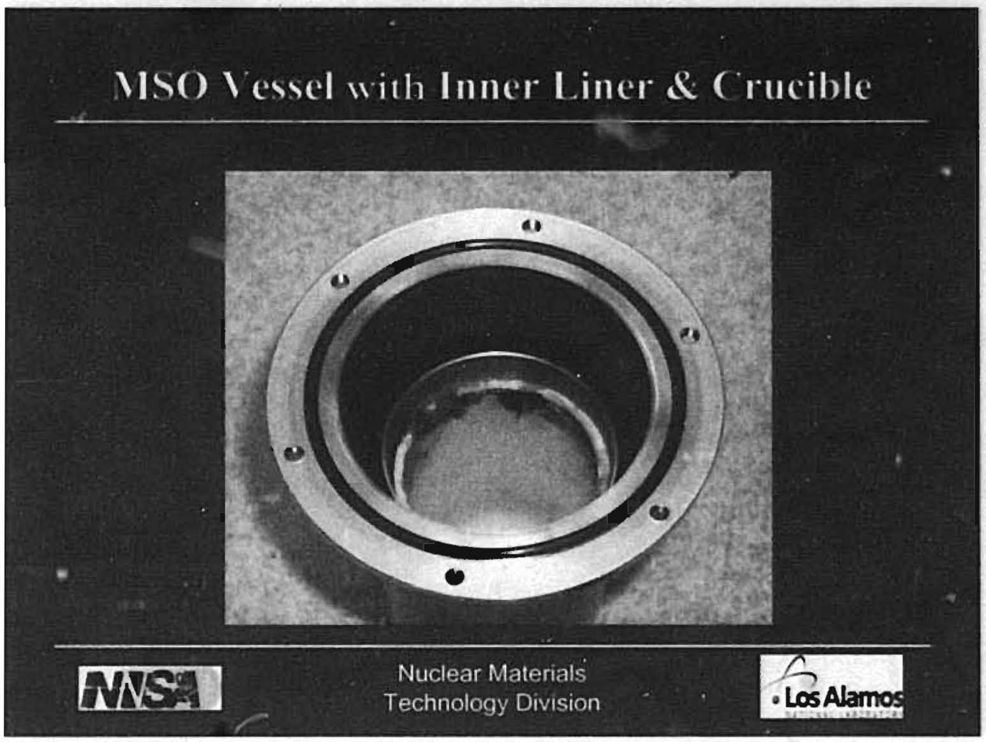
Continuous mode at slow down after proof of principle because getting suitable screwfeeder and new materials lined up was taking time.



Much lower volume air so no need for height.

In batch mode:

1. Shorter. Does not stick out of furnace much. Due to existing authorization. Need to change as little as possible from previous work done in that spot.
2. No downcomer. Just a metal sparge tube.



Crucible sits in liner can in case of breakage.

3. In the batch mode, ash and salt (when new) fill to the top of the crucible. Volume limited ash. Salt viscosity also.

4. Salt must be broken up between runs. Not left in a single plug. Due to mixing properties of the ash and safety considerations. Requires worker exposure.

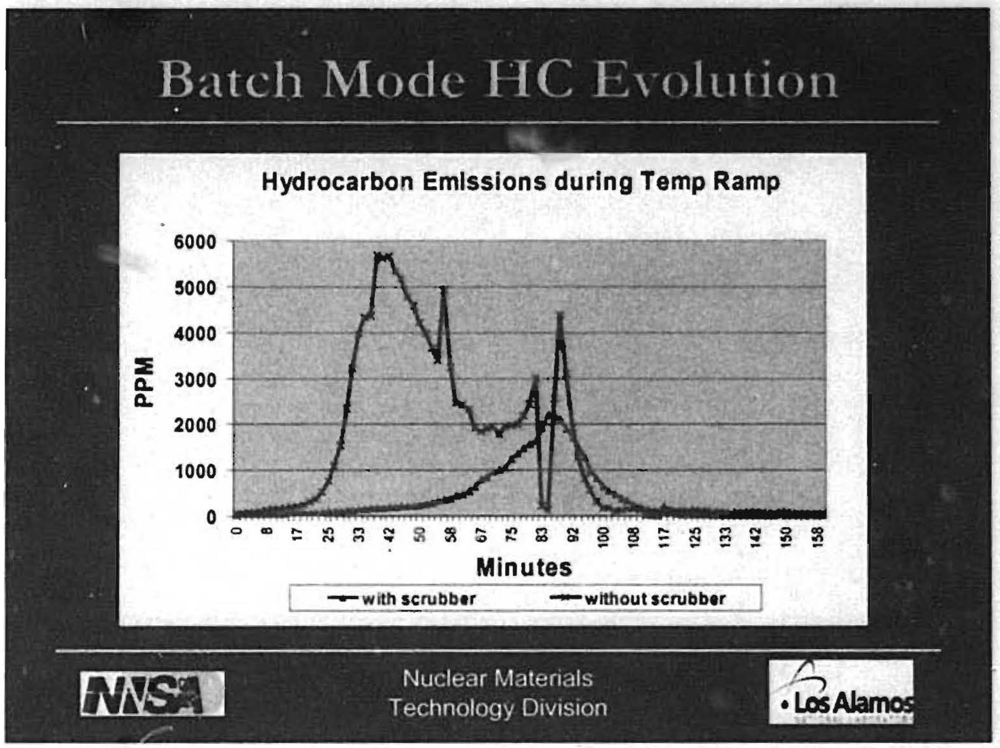
Clearly, a less effective alternative, yet important test of unit in actual glove box conditions. Could do 30-60 g of ash in a batch run. Can do 120 g ash (presently) in same amount of running time, 240 g possible because running time can be extended.

Notes on #4

1.Cannot just lay ash on top, never mixes.

2.Cannot put on the bottom because then we couldn't attach the lid before starting due to sparge tube not being completely at the bottom of the crucible.

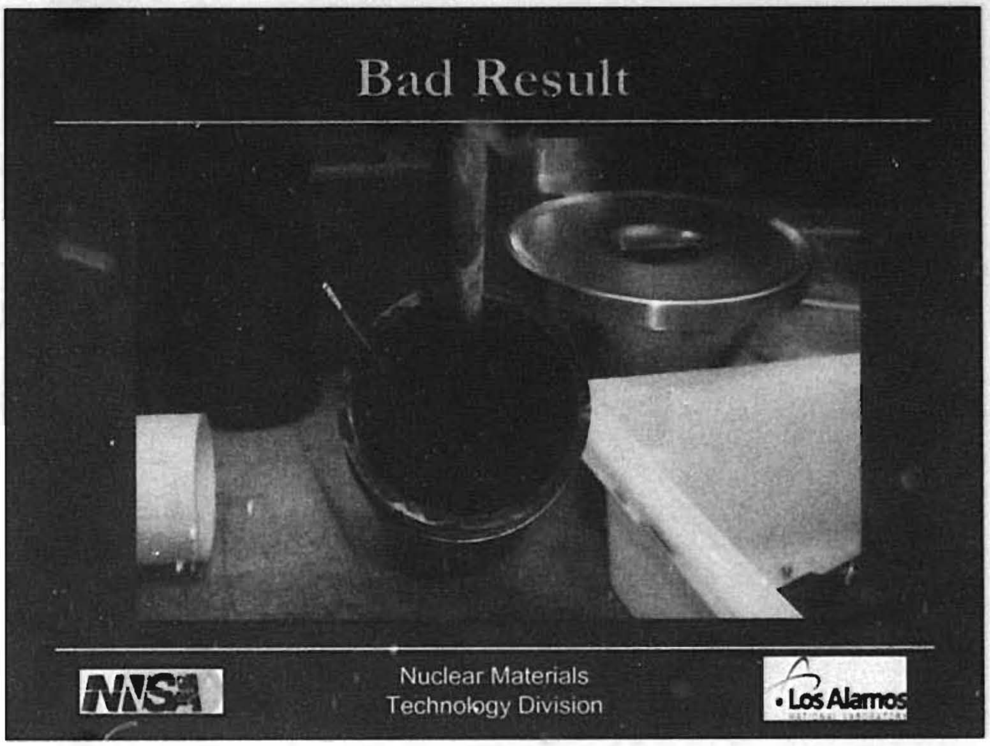
3. Cannot leave sparge tube out, because we do not want to access while hot if possible. Safety.



The run requires a temperature ramp over a period of 4 hr. During this time the ash is repyrolyzed. Temp ramp is done under argon, further HCs come off.

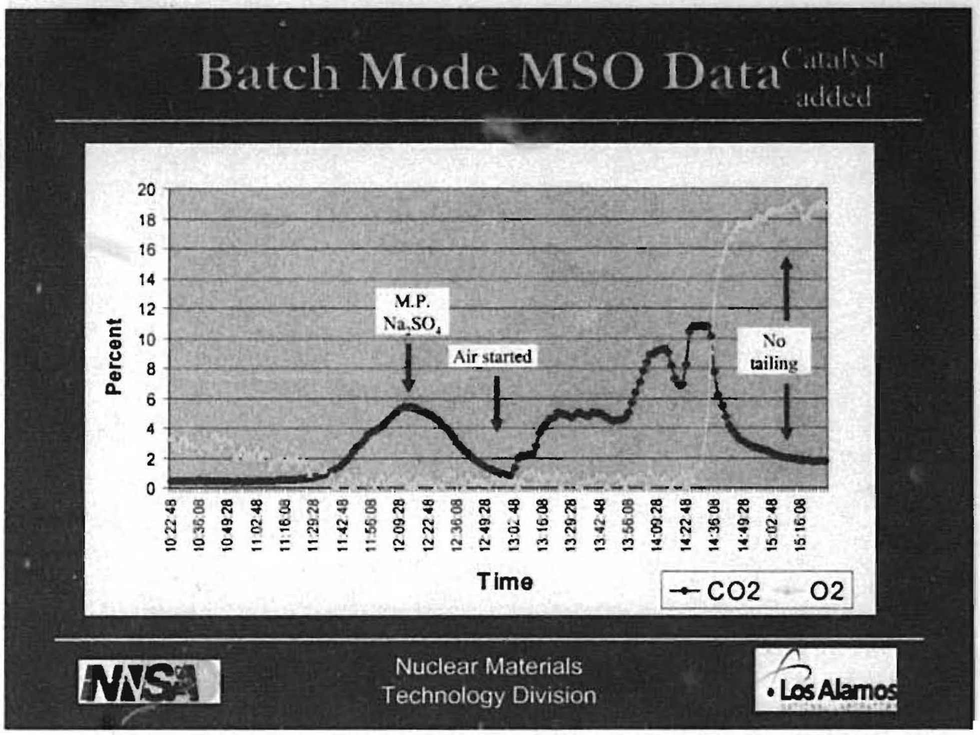
First peak comes off at about 500°C, (peak 520C) second between 650°C and 750°C. Salt is molten at 850°C and higher.

With the use of the simple 4M NaOH scrubber, emissions satisfactorily reduced.



Only problem was incomplete combustion. Crucible with layer of ash

Typically can get the salt plug out with the help of a little water and using the sparge tube like a Popsicle stick to get a purchase on it. In this case, that cannot work.



7/17/03

Addition of sodium sulfate to 1% gives us a more complete reaction and a slightly different profile.

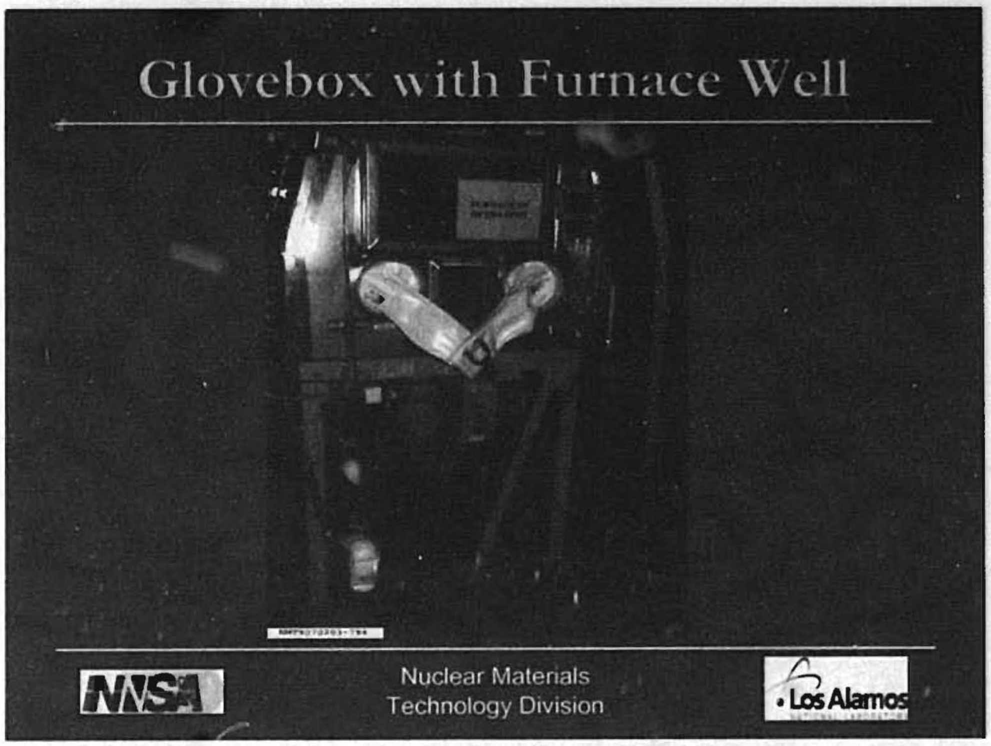
Peak at M.P. sodium sulfate.

Begin processing similarly about 6% CO2, but first of all get no tailing. Don't know what the peaks are but it is reproducible result. The processing time for the bulk of it is about the same as without sulfate.

The sulfate diminishes over time. This is from a batch of salt where the sulfate was added 3 runs ago.

Only part that needed work was the tailing. Left ash on top of the salt. Could not get plug out of crucible. Addition of 1% sulfate worked

30 g ash, 1.8 hr, 10 g sulfate added to salt 3 runs ago.


Glovebox with Furnace Well
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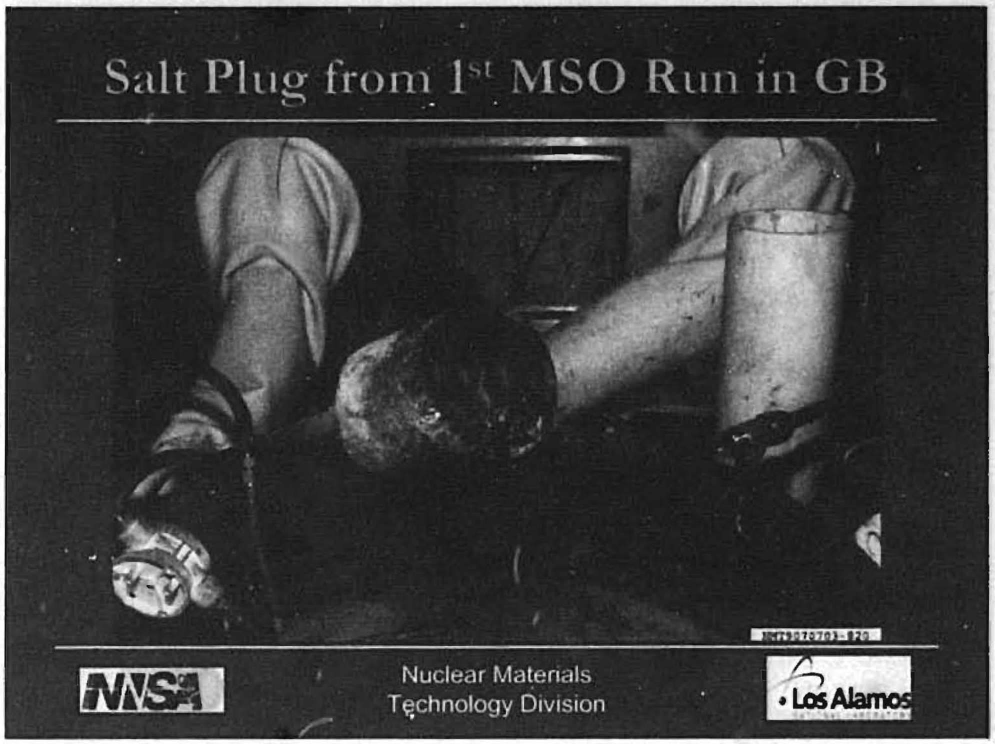
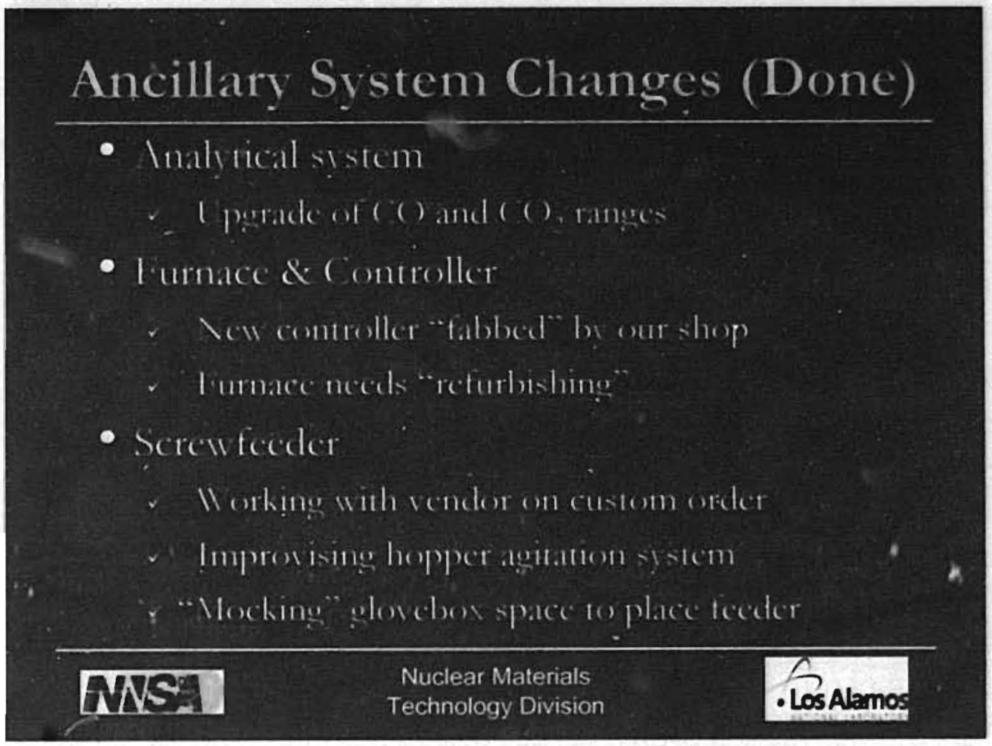
Good to go.



Voila

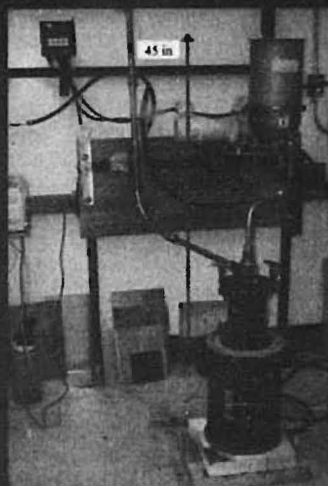
The black bottom is the oxide layer.

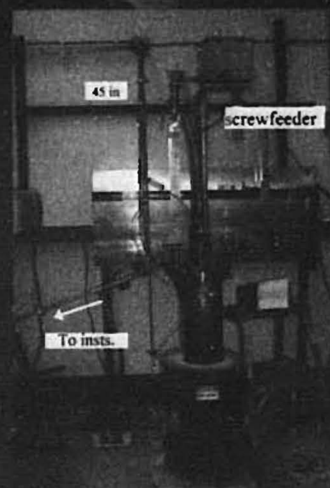
We suspected this would happen, but are glad to prove it again. This makes the recovery easier since we don't need to dissolve all the salt to get at the Pu. Saves salt life.



This slide shows what we were doing at that time. All this has been accomplished. Got the screwfeeder working, furnace back in service, modified the whole shebang up to shorten it.

Continuous Feed Units





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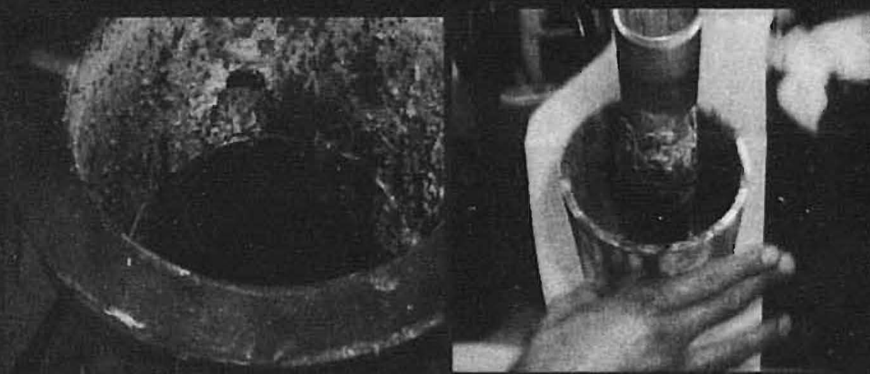
Salt Entrainment



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Bafflization

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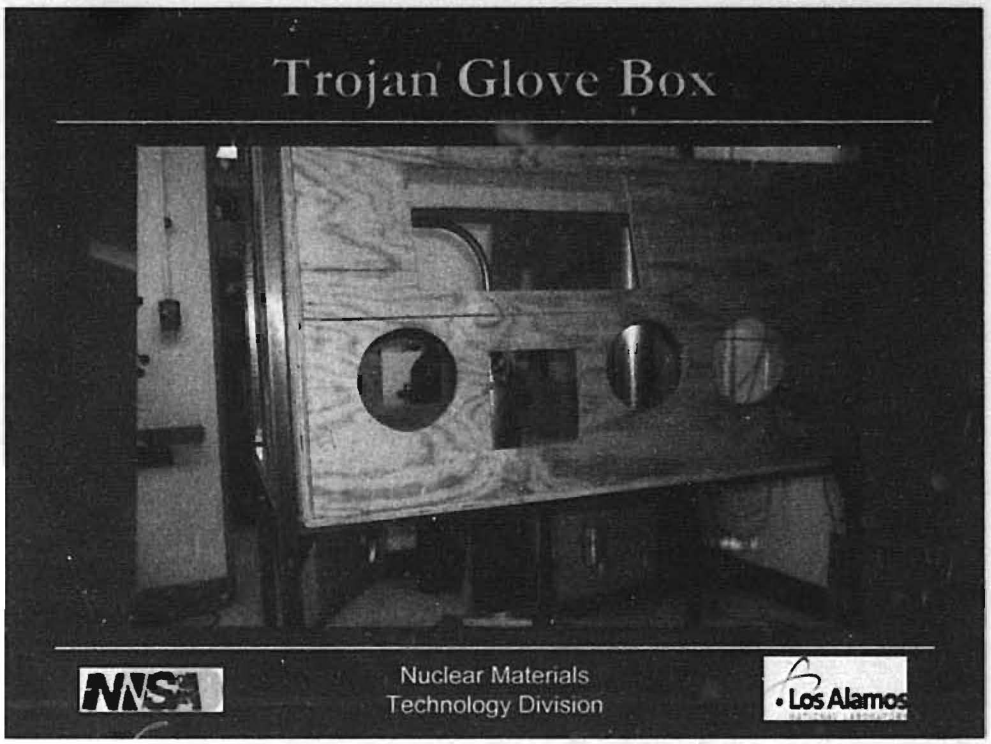
Trojan Glove Box
Nuclear Materials
Technology Division
Los Alamos

Voila

Fits in a Glove Box

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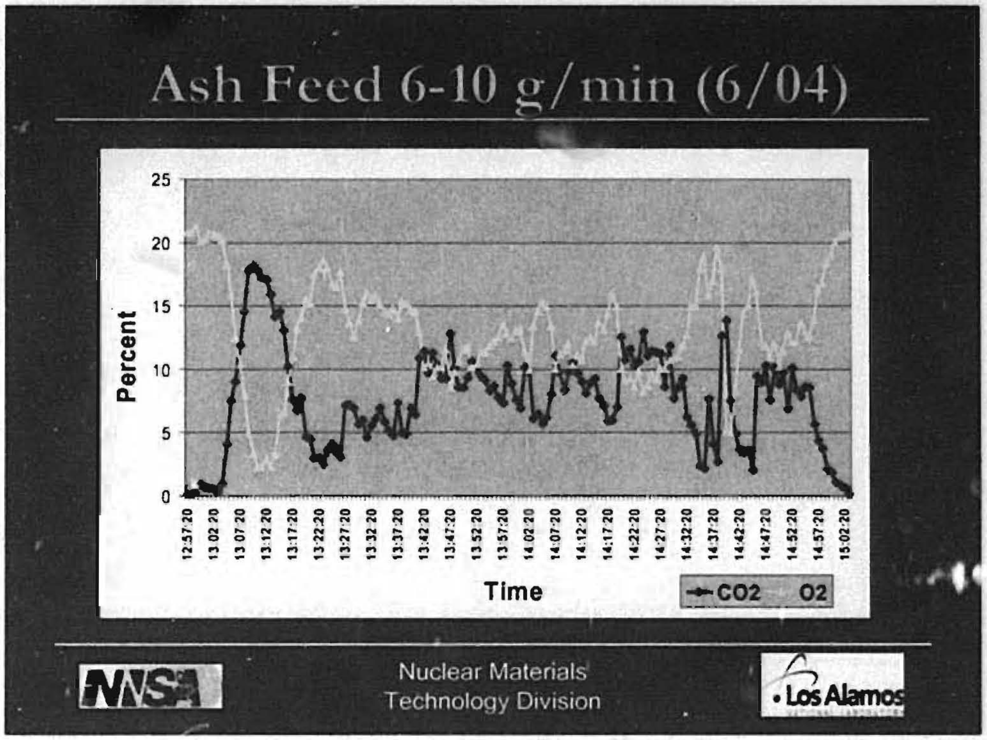
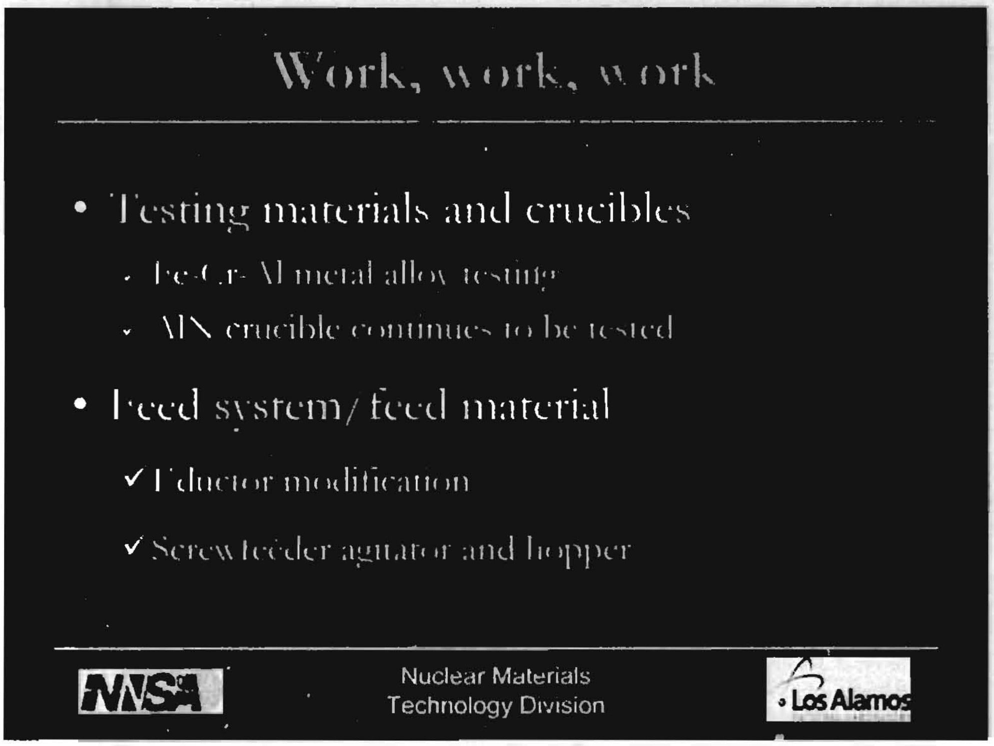


Run of two hours, 6-10 g/min, 2hrs because using too much pyrolysis stuff. 750 g is

Note how there is diminishing CO2, then jumps again. That is from ash diminish in hopper. It is so light it feeds more slowly with less weight above it. Add more to hopper every 15-20 min.



Test materials refers to TiAlC, crucibles to AlN

We have the **screwfeeder** and know it works. We know that we can **feed** at least **1g/min of pure ash**. Both are satisfactory results, but we are contracting with Indian Head to continue looking at possible additives so could feed by gravity, and have improved throughput.

We have learned quite a bit about processing and the limiting boundaries we have to work with. We are also going to work with Indian Head Chemical Engineers to wok on the increased throughput the design and parameterization direction.

Final frontier. Introduction and implementation into the plutonium facility.

Contributors

- C. Dozhier – machinist and designer
- J. Romero, L. Garcia, D. Spengler – Continuous MSO
- K. Krenck, F. Sandoval, R. Hart, D. Herman, J. Matonic – Glovebox MSO Unit
- B. Ewing, M. Lovato – UGS interns on Materials Testing, Plastic Feed Experiments
- M. Vigil – designer

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