ICP-1185

DEVELOPMENT OF A PELLETED WASTE FORM FOR HIGH-LEVEL ICPP ZIRCONIA WASTES

April 1979

Allied Chemical
IDAHO CHEMICAL PROGRAMS

IDAHO NATIONAL ENGINEERING LABORATORY

DEPARTMENT OF ENERGY

IDAHO OPERATIONS OFFICE UNDER CONTRACT EY-76-C-07-1540

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy $4.50; Microfiche $3.00

ICP-1185

Distributed Under Category
UC-70:
Nuclear Waste Managment

Development of a Pelleted Waste Form for High-Level ICPP Zirconia Wastes

by

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Date Published - April 1979

Prepared for the
Department of Energy
Under Contract No. DE-AM07-76ID01540

ABSTRACT

Simulated high-level ICPP zirconia waste calcine is pelletized on a 41-cm diameter pelletizer using 5% bentonite, 2% metakaolin, and 2% boric acid for solids binders and 7M phosphoric and 4M nitric acid as the liquid binders. After heat treatment at 800°C for 2 hours, the pellets are impact resistant and have a leach resistance of 10^{-4} g/cm^2/day, based on Soxhlet leaching for 100 h at 95°C with distilled water.

SUMMARY

The preparation of a pelleted waste form from calcined waste using a rotating disc pelletizer has been tested as a possible candidate process for long-term managment of high-level radioactive defense wastes generated at the Idaho Chemical Processing Plant (ICPP). Simulated zirconia calcine was formed into 3-10mm diameter spherical pellets using a liquid binder of 7M H_3PO_4 - 4M HNO_3 and a solid binder consisting of 5 wt% bentonite, 2 wt% metakaolin and 2 wt% boric acid. The pellets were heat treated at 800°C for 2 hours to form leach-resistant pellets. The pelleted waste has leach resistance nearly as high as that of glass made from the same simulated ICPP wastes.

Extensive pellet binder studies involving a total of 32 pellet compositions with zirconia calcine were made. The work concentrated on binder formulation development to produce a dense, leach resistant pellet after heat treatment. Bentonite was added to the pellets to increase density and react with the Cs on heat treating to impart Cs leach resistance. Metakaolin and boric acid used as solid binders do not materially improve leach resistance, however, they do aid in pellet agglomeration and green strength.

Other binders tested such as SiO_2, Al_2O_3, and $Ca(OH)_2$ had little beneficial effect on the pellets. Colloidal silica does not properly wet the calcine to form uniform pellets without being dissolved in phosphoric acid, while aluminum phosphate solutions are too viscous to spray. Although pellets made using $AlPO_4$ were spherical, they showed no improvement in leach resistance. The reaction of $Ca(OH)_2$ with the acidic liquid binder (H_3PO_4 + HNO_3) was so vigorous that steam was produced causing the pellets to crack. Although $Ca(OH)_2$ may help to reduce leach rates, its effect on processing the pellets are too adverse.

Based on the results of the development study a pilot plant is being built to further evaluate the pelletization process as an alternative for long term waste management.

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I. Introduction

At the Idaho Chemical Processing Plant (ICPP) defense-type nuclear fuels are reprocessed to recover uranium. The resulting high-level wastes are solidified by a fluidized-bed calcination process. Currently there are ∿1700m^3 of calcined high-level wastes stored at ICPP. Compositions of the various types of calcines stored at ICPP are shown in Table I. Properties of zirconia calcine, the most prevalent type, are shown in Table II.

Fluidized-bed calcine a mixture of product (bed) particles and fines, has an angle of repose greater than 80^{o}, thus, the calcine has poor flow characteristics, making it difficult to retrieve if necessary. Fluidized-bed calcine particles are porous and leachable for Cs and Sr, but quite leach resistant for other elements.[3]

Pelletizing is being considered as an alternative to vitrification for disposal of ICPP high-level wastes. By pelletizing, a flowable and easily retrieved product is produced. Also, dispersibility is greatly reduced. Because of larger particle size, surface area is reduced by up to 2000. Pelletizing, therefore produces a product which is less dispersible, less leachable, and more easily retrievable than calcine. Pellets also have a lower preparation temperature than does glass and can be readily converted to other waste forms such as a metal matrix.[4]

The development of a pelleted waste form included extensive pellet binder studies involving a total of 34 pelletizing experiments to evaluate eight different pellet-forming binders. Using a 41-cm diameter disc pelletizer, the zirconia calcine was agglomerated into 3-10mm diameter spherical pellets with the aid of various solid and liquid binders. These solid and liquid binders were examined for ability to react with the calcine to form fracture and leach-resistant compounds after undergoing a heat treating stage. The binders also react with the calcine during pelletizing to form a cement like material, making the pellets resistant to crumbling or fracture when still wet or after being dried at 150 to 200^{o}C.

Table I

COMPOSITIONS OF ICPP CALCINES

Composition (wt%)	Waste Form			
	Alumina	Zirconia	Zr-Na Blend	Electrolytic
Fe_2O_3				10-17
Al_2O_3	82-95	13-17	10-16	57-85
Na_2O	1-3		6-8	1.4-2.7
ZrO_2		21-27	16-19	
CaF_2		50-56	33-39	
Gd_2O_3				6-23
CaO		2-4	13-17	
NO_3	5-9	0.5-2	7-9.5	1-5
B_2O_3	0.5-2	3-4	2-3	2-6
Fission Product & Actinides	0.2-1	0.2-1	0.2-1	0.2-1
Miscellaneous	0.5-1.5	0.5-1.5	0.5-1.5	1-4

Table II

PROPERTIES OF ICPP ZIRCONIA CALCINE

Preparation Temperature, ^{o}C		500-550
Particle Size	Bed, mm diameter	0.1-0.6
	Fines, mm diameter	0.01-0.1
Density, g/cc		1.2-1-6
Nitrate Content, wt% (released between 500-750^{o}C)		1-3
Fission Product Content, wt%		0.2-1
Thermal Conductivity, W/m-K		0.2-0.28
Sintering Temperature, ^{o}C		>800
Major Leachable Elements		Cs, Sr, Cr

II. Description of Pelletizing System

A 41-cm diameter disc pelletizer (Figure 1) with a throughput of 10-80 kg/h was used for the developmental work. The pelletizer is operated by a 0.25 hp motor and the pelletizer disc is the only moving part. Unlike most other agglomerating equipment, the disc pelletizer does not use high pressure to form pellets. A mixture of calcine and solid additives is fed onto the inclined rotating disc. Then a liquid binder is sprayed onto the mixture. As the disc turns, the solids, while rolling and tumbling, grow onto pellets by a snowballing effect. The centrifugal action of the turning disc separates the pellets into three distinct and progressively larger sized streams (Figure 2); a seed stream, a growth stream, and a polishing stream. The polished pellets move to the edged of the disc and spill over to be collected. The product pellets are uniform in size and spherical in shape.

The relative amounts of materials in the three pelletizer streams is affected by the speed and angle of the disc. The angle of the disc can be varied from 40-60^o (in 2.5^o increments) and the speed is continuously variable from a few RPM to over 30 RPM. As the angle of the disc increases, fewer particles are carried over into the seed stream. Less seeds means fewer and larger pellets. Increasing the angle generally increases pellet size, although, at steep angles approaching 60^o some pellets can be crushed and broken. For some feed compositions, the angle of the pelletizer incline can be too steep and pellets may not be formed at all. Decreasing the pelletizer speed reduces the amount of materials in the seed stream thus making fewer and larger pellets. The disc speed is used as a fine tuning device while a change is disc angle causes a greater change in pelletizer operating conditions. Beside disc angle and speed, the locations of the liquid binder spray and solids feed also affect pellet size (Figure 3). The larger the particle size in the stream where the liquid is sprayed, the larger the final pellets will be. The pellet grows because the moist outer pellet layer is coated with dry solids. If the spray is only on the seeds, the medium sized particle in the growth stream cannnot grow because they will not be moist enough to build up additional layers of solids. If the liquid binder spray is located on the pellets in the polishing stream, the pellets will continue to grow. Spraying on the polishing stream will usually yield large, rough surfaced pellets of 10mm diameter or more. Pellet size is similarly although not as dramatically affected by solids feed location. Generally the larger the size of the material in the pelletizer stream where the solids are fed, the larger the final pellet. To produce 4-6mm diameter pellets, the spray is usually located on the growth stream in line with or slightly to the right of the liquid binder spray. Size cannot always be controlled because some solid pellet compositions form only in a very narrow size range. After some time in the polishing stream, experimentally formed pellets roll out of the pelletizer and are collected for further treatment. The pellets formed need to have sufficient green strength to remain intact after falling 30-60 cm. The green pellets should also be free flowing and remain free flowing even when pellet depths of 15-20 cm are reached.

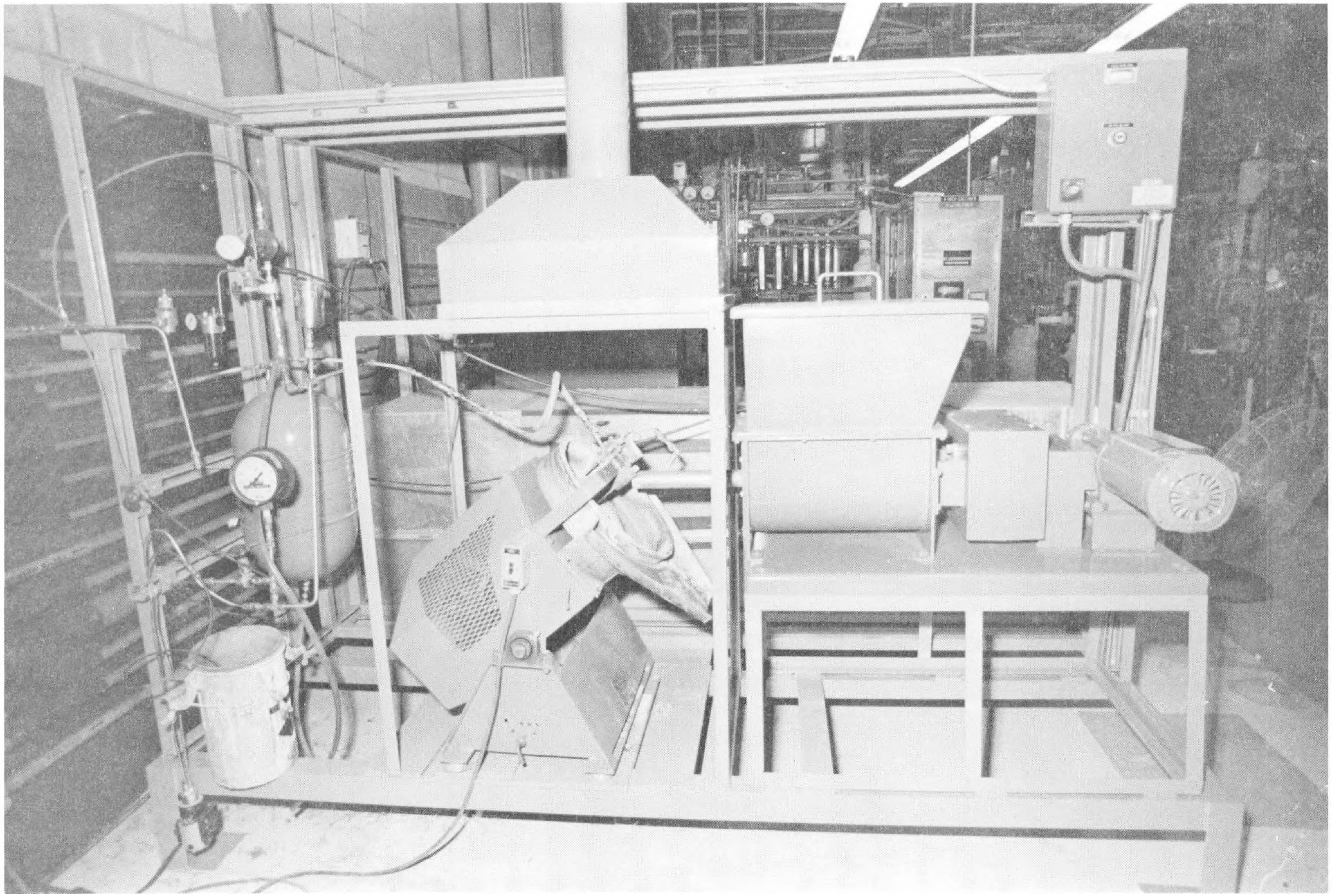

Figure 1. 41-cm Disc Pelletizer Pilot plant Set-up

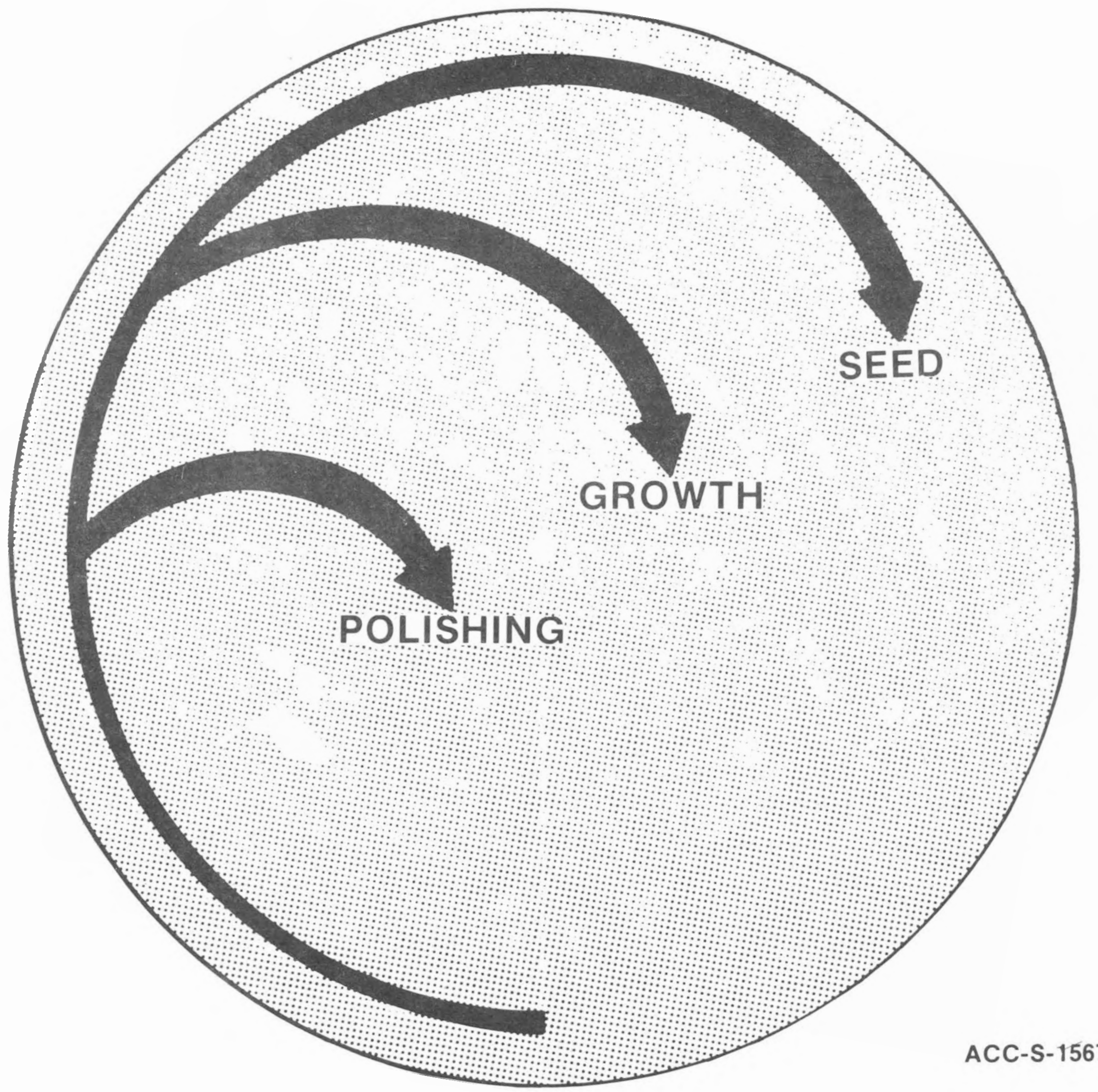

Figure 2. Schematic of a rotating disc pelletizer showing the location of the three pellet-forming streams on the disc.

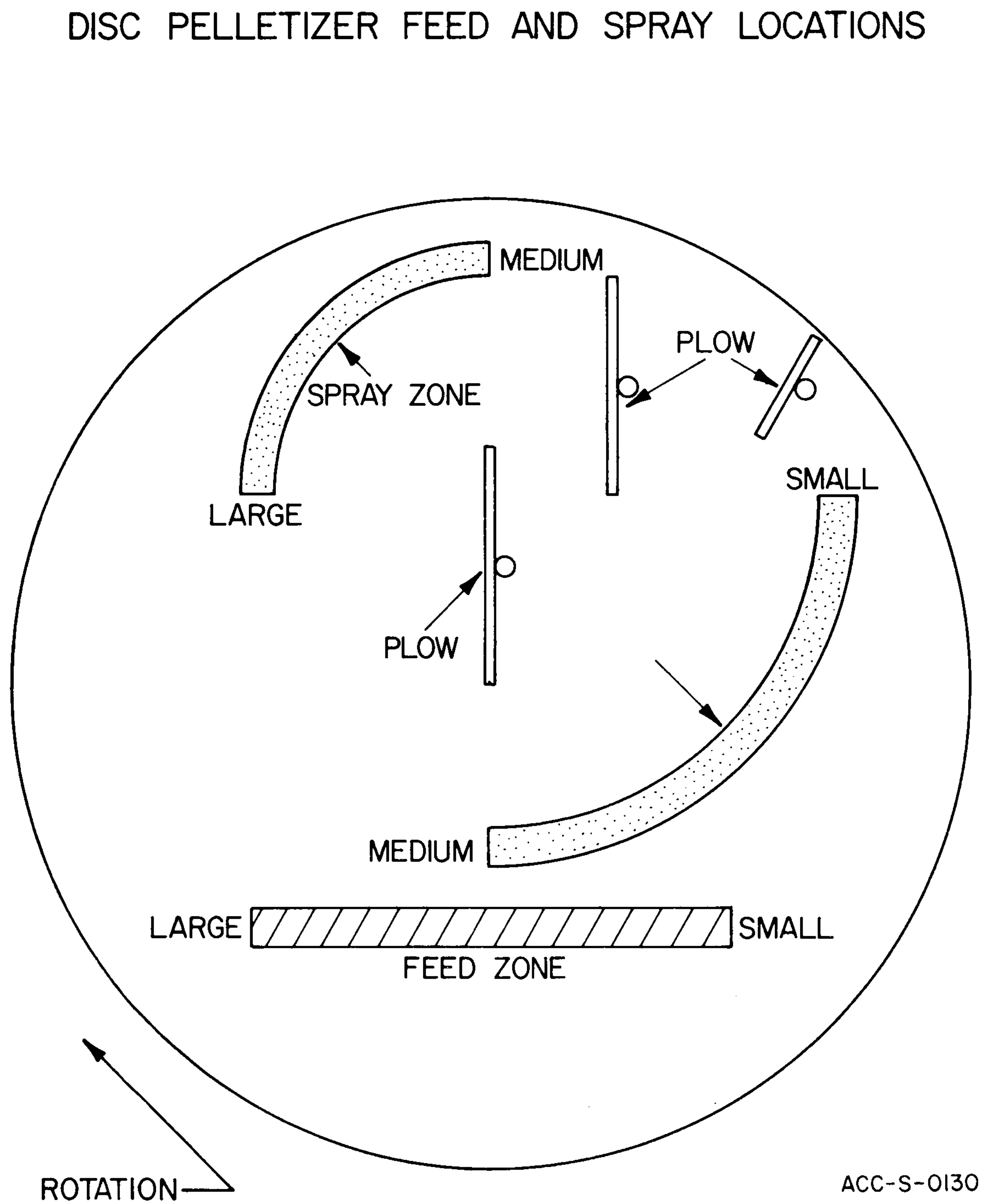

Figure 3. Feed and spray locations on a disc pelletizer

The pelletizer feed systems consists of a solids screw feeder and a liquid spray system. The screw feeder which supplies the mixed calcine and solid binder feed is variable in speed and can deliver flows of less than 100 g/min to more than 2000 g/min. The bin for the solids feed system holds 0.057 m^3 (2 ft^3) of solids. Two systems have been used to spray the liquid binder. One system regulates the air pressure in a pressurized tank to control the liquid flow rate (Figure 4). The other liquid feed system uses a variable speed gear pump to deliver pressures up to 0.55 MPa and flows up to 0.5 l/min. To measure liquid binder flows, a bearingless turbine meter is used. The orginal rotor would not stand up to the acid liquid binder so a new rotor was fabricated. The new rotor in the turbine meter is made from Macor*, a machineable glass ceramic, resistant to acidic solutions.

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* Macor is a trademark of Corning Glass Works

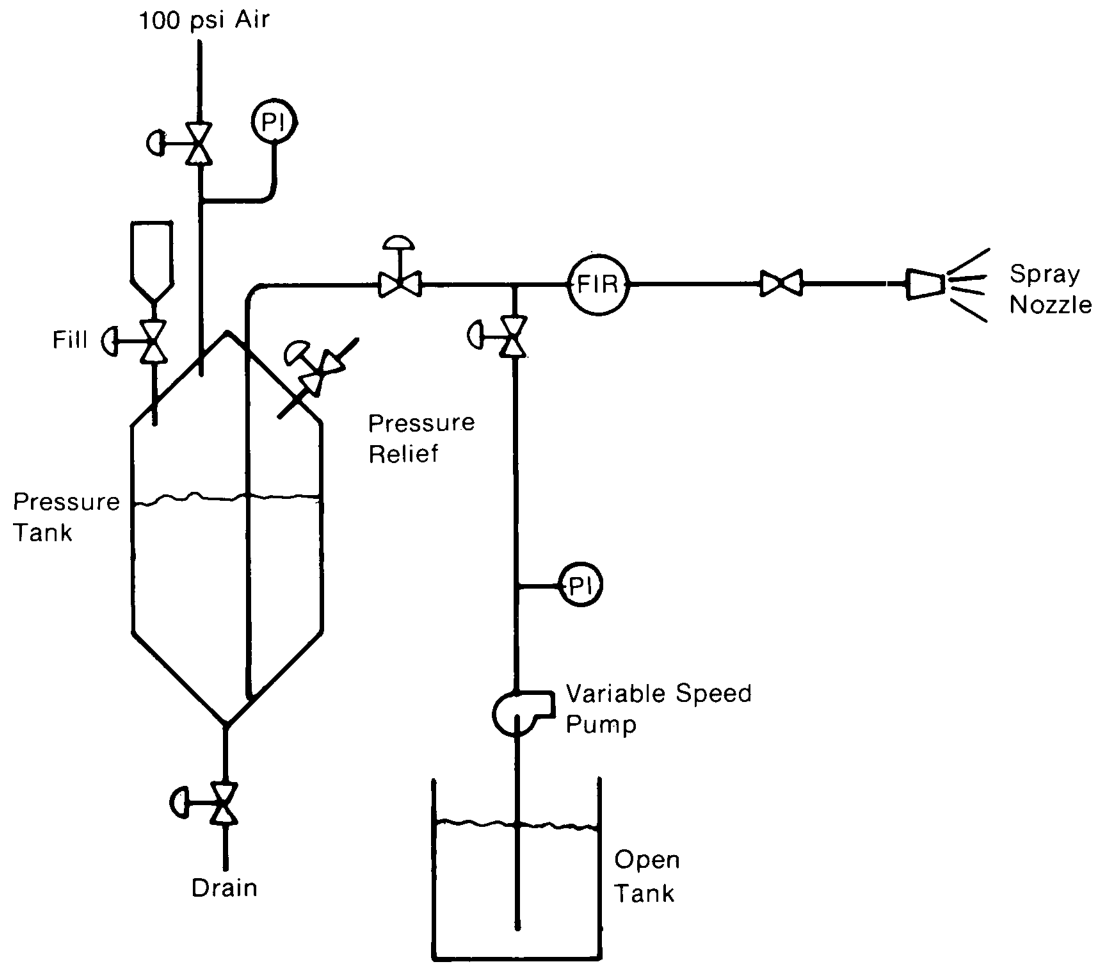

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Figure 4. Schematic of the liquid feed system for the rotating disc pelletizer

III. Pellet Binder Studies

A. Introduction

Zirconia calcine can be pelletized on the disc pelletizer using only water as a binder, but it is a poor binder producing flakey pellets of limited strength with leach resistance no greater than calcine. By using various combinations of solid and liquid binders, pellets can be made with much better properties. The leach resistance of the pellets is improved by the use of binders that react with the soluble or leachable materials in the calcine to form insoluble compounds. These reactions normally take place during heat treatment of the pellets at 800-850°C for two hours. Concentrations ranges of the pellet binders evaluated are given in Table III.

B. Liquid Binders

1. Phosphoric acid

Phosphoric acid has been shown to react with most of the metal oxides in the calcine to form stable and refractory compounds.[5] The two primary reasons for using H_3PO_4 as a liquid binder are 1) to form quick setting aluminum (present in the calcine) phosphate cements which impart green and dried strength to the pellets, and 2) to react with the calcine to form insoluble phosphate compounds to increase the pellet leach resistance. Phosphoric acid concentrations as high as 11 molar were tested. Concentrations above 9M are not useful because the liquid binder is too viscous to form an atomized spray (Figure 5). Spraying high molarity H_3PO_4 in a solids stream results in locally high amounts of liquids, large lumps and poor quality pellets.

The effectiveness of H_3PO_4 in the liquid binder is evident in both the physical strength and chemical leach resistance of the pellets. Pellets made with phosphoric acid in concentrations <5M did not agglomerate well and tended to be irregularly shaped, fragile and of generally poor quality. With H_3PO_4 concentrations above 5M the physical strength of the pellet was good and the calcine agglomerated well, yielding uniform and spherical pellets (Table IV). Physical considerations such as high binder viscosities or poor pellet strength limited experimental H_3PO_4 concentrations to between 5-9M. Pellet leach resistance, both based on Cs, reached a maximum at 7M H_3PO_4. A concentration of 7M H_3PO_4 also consistently yielded uniform pellets with good all around physical properties. Therefore 7M H_3PO_4 is considered the most practical liquid binder concentration to form a pelleted waste with zirconia calcine.

2. Nitric Acid

Nitric acid is used in conjuction with H_3PO_4 as a liquid binder. Using only H_3PO_4 produces pellets which are flaky and mushy. Since the second ionizing proton of H_3PO_4 is not acidic (pKa_2= 7.21) HNO_3 is added to increase the binder acidity, resulting in better reaction with the basic calcine, and decreasing the liquid binder viscosity. Also phosphate-

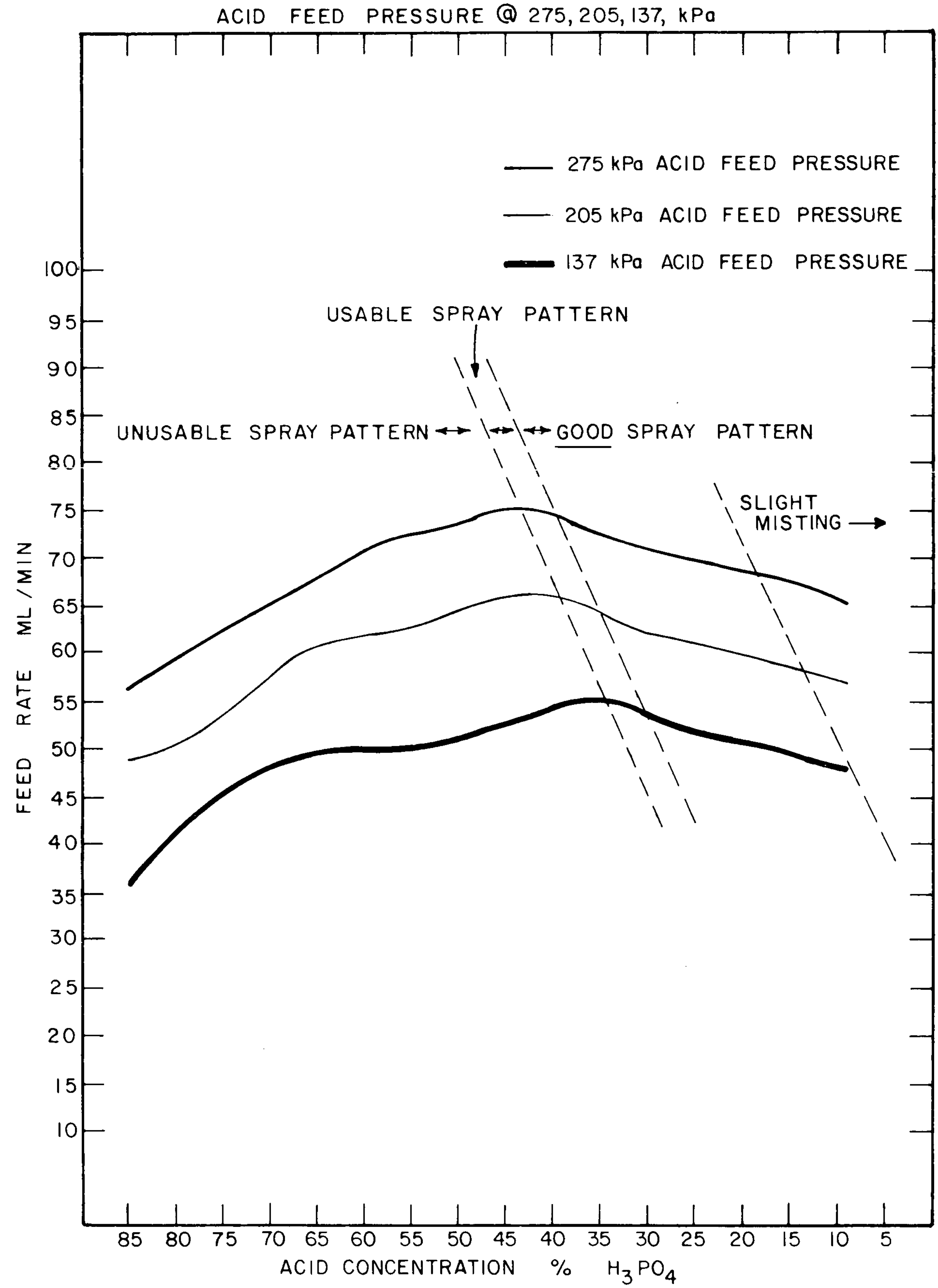

Figure 5. Spray Pattern and Flow Rates of IX Conejet Nozzle vs. Phosphoric Acid Concentration at Three Pressures.

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Table III

Concentration Ranges of Pellet Binders Tested

Solid Binders				Liquid Binders			
Bentonite wt%	Boric Acid wt%	Metakaolin wt%	$Ca(OH)_2$ wt%	H_3PO_4 M	HNO_3 M	SiO_2 M	$AlPO_4$ as Al_2O_3
3-5	2-10	2-20	5-20	1-11	1-4	1.5-4	1-2.5

Table IV

Effects of H_3PO_4 Concentration on Pellet Properties

H_3PO_4 M	Shape Characteristics	100 H Soxhlet Leach Rates g/cm²/day Bulk	Cs
1	no pellets formed		
2	no pellets formed		
5	rough, some odd shapes	1.4×10^{-3}	2.4×10^{-2}
7	spherical smooth	7.3×10^{-4}	6.8×10^{-3}
9	oblong, rough	1.9×10^{-3}	2.3×10^{-1}

metal oxide reactions form better cements under acidic conditions.

Liquid binders consisting of 7M H_3PO_4 and greater than 4M HNO_3 are too viscous to spray well. Nitric acid concentrations between 1-4M aid in producing leach resistant pellets with good physical and pelletizing properties (Table V). Four molar HNO_3 gives the highest bulk leach resistance while 1-2M HNO_3 may produce slightly better leach resistance for Cs. However pellets made with 4M HNO_3 appeared smoother and more spherical. A liquid binder consisting of 4M HNO_3 and 7M H_3PO_4 seems superior to other combinations tested for producing zirconia pellets.

3. Silica

Silica was also tested as a liquid binder. Silica was added in an attempt to form a pollucite type ($CsAlSi_2O_6$) compound during sintering of the pellets. Pollucites, if formed, are leach resistant. If silica could replace some or all the H_3PO_4 used as a pellet binder, the pellets would also be more easily converted to glass, if that ever became necessary.

The form of the silica used was DuPont Ludox HS 30% Collidal Silica. Colloidal silica has a much lower viscosity than does sodium silicate, a lower level of sodium, and it can be mixed with 3M H_3PO_4 without gelling. For a liquid binder, three forms of colloidal silica were used: 1) 30 wt% SiO_2 (5M), 2) 15 wt% SiO_2 (2.5M), and 3) a solution of 3M H_3PO_4 and 2.4M SiO_2.

Four pellet forming runs were tried using silica in the liquid binder. Two binders, 30% and 15 wt% colloidal SiO_2, would not form pellets on the pelletizer. The colloidal silica did not wet the calcine particles or help them agglomerate and form pellets. The basic (pH= 9.8) colloidal silica would not react with the basic metal oxides which make up the calcine. The colloidal silica could be mixed with 3M H_3PO_4 without gelling. Time to gel for a solution of 3M H_3PO_4 - 2.4M SiO_2 held at room temperature is greater than 48 hours. As a liquid binder, the combined acid-silica solution more readily wetted the calcine and solid binder feed mix than silica alone. The pellets formed were more uniform than those using just the silica solution, though they were still rough surfaced, of variable and often odd shapes.

After four relatively unsuccessful pellet runs, colloidal silica and silica-H_3PO_4 solutions were abandoned as a possible pellet binder. Almost all the pellets formed were not spherical or of inconsistent size. The silica-H_3PO_4 binder also formed pellets which were more friable and dusty than the pellets made with H_3PO_4-HNO_3 binders. The leach resistance of the silica pellets, especially for Cs, appeared to be much poorer than for similar pellets made using a H_3PO_4-HNO_3 binder (Table VII). Silica did not pelletize well or improve pellet properties.

4. Alumina

Aluminum oxide slurried with phosphoric acid, and aluminum phosphate, were tested as possible liquid binders. Aluminum phosphate reacts with metal oxides to form cohesive products. In addition, aluminum greatly increases the bonding power of phosphoric acid.[5] By using an aluminum phosphate liquid binder, the calciner particles could possibly be coated with an aluminum phosphate cement material. This could increase leach resistance and possibly increase the strength of the pellet.

Table V

Effect of Nitric Acid Concentration on Pellet Properties

HNO_3 M	Shape Characteristics	Leach Rate g/cm²/day Bulk	Leach Rate g/cm²/day Cs
0	irregular, off sized poor agglomeration	6.8×10^{-4}	7.7×10^{-3}
1	small, flat shapes many lumps	2.9×10^{-3}	2.9×10^{-3}
2	small, mostly spherical	5.0×10^{-4}	6.52×10^{-3}
4	smooth surfaced spherical	3.5×10^{-4}	9.5×10^{-3}

Table VI

Properties of Silica as a Liquid Binder

Run No.	Liquid Binder	Pellet Characteristics
15a	Ludox HS 30*(30 wt% SiO_2	1.6-3.2 diameter, flat irregular, rough, not really pellets
16a	15% SiO_2, HS 30% diluted with H_2O	no pellets formed
17c	12% SiO_2 + 3M H_3PO_4	6-6 mm diameter rough, uneven pellets
18c	12% SiO_2 + 3M H_3PO_4	3-5mm rough, irregular

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* Ludox is a trademark of DuPont

Table VII

Comparison of Pellets Made Using SiO_2 and H_3PO_4-HNO_3 as Liquid Binders

Solids Composition	100 H Soxhlet Leach Rate with SiO_2 binder g/cm^2/day		100 H Soxhlet Leach Rate with H_3PO_4-HNO_3 binder g/cm^2/day	
	Bulk	Cs	Bulk	Cs
Calcine + 5 wt% H_3BO_3 5 wt% Bentonite and 5 wt% Metakaolin	4.0×10^{-4}	4.45×10^{-2}	2.9×10^{-4}	4.0×10^{-3}
Calcine + 5 wt% H_3BO_3 and 5 wt% Bentonite	5.9×10^{-4}	1.06×10^{-1}	2.7×10^{-4}	1.9×10^{-2}

Table VIII

Comparison of the Leach Resistance of Pellets Made From Slurried Al_2O_3 and Liquid $AlPO_4$ and 7M H_3

Binder	100 h Soxhlet Leach Rate			
	Bulk	Cs	Sr	B
7M H_3PO_4, 1M HNO_3 14 wt% slurried Al_2O_3	1.0×10^{-3}	6.0×10^{-3}	1.2×10^{-3}	2.7×10^{-3}
7M H_3PO_4, 2M Al^{+3}	7.2×10^{-4}	4.5×10^{-2}	7.2×10^{-3}	1.3×10^{-3}
7M H_3PO_4, 1M Al^{+3}	2.1×10^{-4}	4.1×10^{-2}	6.1×10^{-4}	8.8×10^{-4}
7M H_3PO_4, 2M HNO_3	4.7×10^{-4}	4.0×10^{-3}	1.1×10^{-5}	5.7×10^{-4}

Alumina by itself is basic, and must be neutralized with H_3PO_4 or it will not react with the calcine to form cement like compounds.

Attempts to prepare an aluminum phosphate liquid binder using alpha Al_2O_3 and a solution of H_3PO_4 and HNO_3 failed. Alpha Al_2O_3 is practically insoluble in H_3PO_4. A slurry (255 g/l) using minus 2000 mesh (less than 0.074 mm) Al_2O_3 powder in a solution of 7M H_3PO_4 and 1M HNO_3 was tried, but proved impractical. The slurry tended to rapidly plug the liquid binder spray nozzle. The longest run time before plugging was ~15 minutes. The few pellets formed were oblong but smooth surfaced. Although the pelletizer was not operated at steady state the pellets did have better Cs leach resistance than did pellets made with the same solids feed and a 7M H_3PO_4 - 2M HNO_3 liquid binder (Table VIII).

Because of the difficulties in spraying the slurried Al_2O_3 binder another method of making an aluminum phosphate liquid binder had to be found. An aluminum phosphate solution was prepared by dissolving powdered aluminum metal in H_3PO_4. This solution was felt to be more reactive than the Al_2O_3 slurry, so less Al^{+3} was used. At room temperature aluminum metal dissolves fairly slowly in H_3PO_4, but at temperatures near 90°C the dissolution is very fast. To dissolve the aluminum, the 7M H_3PO_4 is heated to 100-110°C and small amountes of the powdered aluminum are periodically added until a 1 or 2M solution is made. Aluminum phosphate in 7M H_3PO_4 is very viscous. No more than 2M Al can be used before the solution is unsprayable.

The leach resistance for pellets made using liquid aluminum phosphate and the slurried Al_2O_3 are compared to pellets with the same solids composition and 7M H_3PO_4 and 2M HNO_3 as a liquid binder (Table VIII). The two runs made with liquid $AlPO_4$, 2M Al and 1M Al, had high Cs leach rates. The run made with slurried Al_2O_3 had a Cs leach resistance comparable to the 7M H_3PO_4-2M HNO_3 binder, but resistance to bulk, Sr, and B leaching was lower. Because of poor leach resistance and processing difficulties, Al_2O_3 and $AlPO_4$ are not recommended as liquid pellet binders for zirconia calcine.

C. Solid Binders

1. Bentonite

Bentonite was tested as a solid binder to increase Cs leach resistance. Bentonite ($(Mg\ Al)_3\ (AlSi)_4\ O_{10}\ (OH)_2$) is an absorptive and colloidal clay used mostly in the paper industry as a filter. Bentonite reacts with Cs, Sr, and other active metal oxides to form insoluble, leach resistant compounds. The Cs or Sr is taken into the bentonite structure by ion exchange.[8] By mixing bentonite with the calcine prior to feeding to the pelletizer, the bentonite becomes thoroughly mixed throughout the pellets. By heat treating the pelleted calcine, bentonite reacts with the Cs to chemically fix it in the pellet structure.

When adding solid binders the object is to use enough binder to impart strength and react with the desired calcine components, but not so much as to greatly increase the total volume of solids. Generally solid binders were kept under 20 wt% of the pellet weight. Solids containing 20% or more boric acid, $Ca(OH)_2$ or metakaolin did not pelletize. The stoichiometric amount of bentonite needed in the pellet to bond all the Cs and Sr is

∿1.0 wt% of the calcine. Bentonite amounts above 5 wt% tend to cause the green pellets to become sticky and non-free flowing. The levels of bentonite used were 3 and 5 wt%. Overall pellet leach resistance increased about a factor of 3 by bentonite addition whereas the Cs and Sr leach resistance increased by a factor of 4 to 5 (Table IX). For 100 hr soxhlet leaches, Cs and Sr leach resistance was highest at bentonite concentrations of 5 wt%.

A factor which appears to keep the leach resistance for Cs around 10^{-3} $g/cm^2/day$ for the pellets is the large size of the calcine bed particles. The calcine bed particles, which range in size from 0.14-0.50 mm diameter, contain soluble Cs in the interior volume of the particle. Binder penetration of the particles during heat treatment is apparently insufficient to completely immobilize the Cs. Because the heat treated pellets are porous, the soluble or unreacted Cs eventually leaches. To correct this, the size of the particles may have to be reduced, or the pellets may have to be further coated to eliminate pellet porosity.

1. Metakaolin (Calcined Kaolin)

Kaolin ($Al_2Si_2O_5(OH)_7$) is also on absorptive clay commonly used as a filler. The calcined or dehydrated kaolin (metakaolin) can react with Cs much like bentonite. The calcined clay is used because it is generally more reactive than the hydrated clay.[7] Metakaolin begins reacting with Cs at temperatures as low as 500°C. In testing, as much as 20 wt% metakaolin was added to the calcine. Testing indicated that more than 10 wt% metakoalin made the calcine mixture very difficult to pelletize because metakaolin is not easily wetted (Table X) causing poor agglomeration.

Metakaolin in small quantities (5 wt% or less) will fill voids between calcine particles and enhance pelletization. For appearance and strength of the pellet a few percent metakolin is beneficial. Small additions of metakaolin also increases leach resistance, especially Cs leach resistance. The bulk leach resistance of pellets containing 2 and 5 wt% metakaolin is simlar, with the 2 wt% pellets possibly having the better Cs leach resistance. Because metakaolin improved these physical properties of the pellets, 2 wt% metakaolin is recommended in the pellet binder composition.

3. Boric Acid

Boric Acid was tested as a solid binder, over the range of 0-10 wt%, for many of the reasons H_3PO_4 was tested as a liquid binder; potentially improved pellet strength and leach resistance. The experiments show that boric acid increases the pellet green strength because it reacts with the basic oxides in the calcine. Boric acid was also added to lower the sintering temperature of the pellet and to aid in decreasing the pellet porosity during heat treating. Boric acid concentrations of 10 wt% produced pellets with good green and dried strength, although heat treated strength is not improved (Table XI). Boric acid does not appear to improve pellet leach resistance. The boric acid apparently did not increase sintering or lower pellet porosity enough to reduce leach rates.

Table IX

Effect of Bentonite on Pellet Leach Resistance

Bentonite Content wt%	Soxhlet Leach Resistance, $g/cm^2/day$ Cs	Sr	Bulk
0	1.02×10^{-2}	3.15×10^{-4}	7.9×10^{-4}
3	4.53×10^{-3}	2.8×10^{-4}	9.97×10^{-4}
5	1.88×10^{-3}	8.0×10^{-5}	2.89×10^{-4}

Table X

Effect of Metakaolin on Pellet Formation and Leach Resistance

Metakaolin Content	Pellet Characteristics	Leach Resistance, $g/cm^2/day$ Bulk	Cs
20	very small, irregular	not leached	
10	small, irregular soft	9×10^{-4}	
5	smooth spherical	4.7×10^{-4}	7.3×10^{-3}
2	smooth spherical	4.8×10^{-4}	2.6×10^{-3}
0	rough surfaced, irregular	2.7×10^{-4}	1.9×10^{-2}

Table XI

Boric Acid added	Pellet Strength % remaining intact after dropping 10M dryed	Heat treated	100 H Soxhlet Leach Resistance $g/cm^2/day$ Bulk	Cs
10%	100	72	3.8×10^{-3}	5.0×10^{-2}
5	88	86	7.9×10^{-4}	3.8×10^{-2}
0	86	74	5.0×10^{-4}	6.5×10^{-3}

Small amounts of boric acid, much like the solid binder metakolin, improve some physical properties of the pellets. Since boric acid improves pellet green and dried strength, and because even small amounts help make smooth pellets, the use of 2 wt% boric acid is recommended in the solid binder.

4. $Ca(OH)_2$

Slaked lime or $Ca(OH)_2$ was tested as a solid pellet binder in four runs. Calcium hydroxide or calcium oxide will react, similarly to Al_2O_3, with H_3PO_4 and form stable cold setting cements.[9] By using $Ca(OH)_2$ in the solids mixture and a liquid binder containing H_3PO_4, the cement forming reaction was expected to possibly improve pellet strength and leach resistance.

Concentrations as high as 20 wt% $Ca(OH)_2$ were tested in pellets (Table XII). Bulk leach rates were low, but pelletizing properties were poor. Lime being a very strong base reacts too vigorously with the H_3PO_4. The reaction heats the pellets and causes the evolution of steam. The steam causes the pellets to swell, and to become porous and friable. Many of the pellets cracked during pelletizing or upon drying. With concentrations as low as 5 wt%, the lime still made the formation of uniform, spherical pellets impossible. Even though it may improve leach resistance, lime is not recommended as a pellet binder for zirconia calcine because of the adverse effects upon the formation of pellets.

Table XII

Effect of Calcium Hydroxide on Pellet Formation and Leach Resistance

$Ca(OH)_2$ wt%	Shape Characteristics	100 h Soxhlet Bulk Leach Resistance $g/cm^2/day$
20	mostly spherical, 20-30% cracked upon drying, rough surfaced	3.0×10^{-4}
10	small, odd shaped rough surfaced	1.7×10^{-4}
5	some very large, many very small fairly smooth but very irregular	not leached

Table XIII

Properties of Pelleted Zirconia Waste

Pellet diameter mm	Bulk density g/cc	Compression Strength MPa	Soxhlet Leach Rate $g/cm^2/day$ Bulk	Cs	Drying temperature ^oC	Heat treatment Time & Temp
3-10	1.0-1.4	3-6	10^{-4}	10^{-3}	200	2 hours @ 800-850^oC

IV. Discussion and Further Properties of Zirconia Pellets

In establishing a pelleted waste form from zirconia calcine, many different properties were investigated. Properties necessary for long term storage of a high-level waste are not well defined. Current regulations state only that the waste must be in a stable solids form.[10] Efforts were made to prepare pellets which would have sufficient strength to be pneumatically transportable. Pellet leach resistance compatable to glass prepared with high-level waste was considered desirable. Much of the binder development work centered on improving pellet leach resistance. Preparation of pellets 3-10 mm in diameter was a goal. Smaller or larger pellets are undesirable because smaller pellets have large surface areas and larger pellets require more energy to transport and are subject to increased attrition. Table XIII lists the ranges of properties of zirconium pellets prepared with recommended binders.

To impart leach resistance, the pellets must be heated to high temperatures for the binders to react with the calcine. These reactions must occur in the semi solid state to prevent fusing together of the pellets. Heat treating serves two basic needs; 1) it drives off volatiles, such as H_2O and NO_x, which are present in the calcine and in the binders used, which could otherwise pressurize storage containers, and 2) it supplies the high temperature media needed for reactions between binders and leachable materials, such as Cs and Sr which are present in the calcine. The effects of heat-treatment temperatures on leach resistance as determined by both soxhlet and brine leaches is shown in Table XIV for pellet composition P-3 (10 wt% H_3BO_3, 5 wt% metakaolin, 11M H_3PO_4, 4M HNO_3). The brine solutions A, B, C are based on information supplied by Sandia Laboratories on brines typical of an area near a salt strata being considered for a waste repository. The compositions are listed in Table XV.

Heating the pellets for two hours at 750-800°C produces leach rates equilvalent heating for one hour at 850-900°C (Figure 6). Heat treatment temperatures, though, cannot be based solely on leach resistance. At 900°C some pellets would soften and agglomerate. Pellets also contain Cs which if unbound can be volatilized at high temperatures. Currently studies on off-gas released during heat treating of pellets show no apparent Cs volatility problems. When completed, studies will determine under what conditions of temperature and heating rates materials such as Cs and Hg volatilize. Information gathered from off-gas studies could greatly affect heat-treating times and temperatures.

Pellet properties and the formation process will be compared to glass and other candidate waste forms to determine the value of pellets as a waste form. Table XVI compares the properties of pellets and glass made with zirconia calcine. Calcine has the advantage of minimum processing, while glass has the greates leach resistance. Still, pellets have a high waste content, intermediate leach resistance and low preparation temperatures. Also, pellets are compatible with current ICPP solid waste storage practices. A pelleted waste form could reduce dispersability and leachability compared to calcine stored at ICPP.

Table XIV

Effect of Heat Treatment Temperature on Bulk Leach Rate for Pellet Composition P-3*

Treatment Conditions Time h	Temp °C	Leach Rate, $g/cm^2/day$ Brine Solutions, 25°C A	B	C	wt loss (-) or Gain (+) in 19 hr Acid Leach 25°C	Caustic Leach, 25°C	Dist. H_2O @ 95°C
1	700	-	-	-	--	--	-2.1E-3
2	700	-	-	-	-1.3E-3	-7.5E-4	-1.1E-3
1	750	+1.3E-2	+1.3E-2	-8.7E-5	-2.4E-3	-2.6E-4	-1.1E-3
2	750	+1.3E-2	+1.5E-2	-5.8E-5	-1.6E-3	-4.6E-4	-7.2E-4
1	800	-	-	-	-2.7E-3	-6.3E-4	1.0E-3
2	800	+1.1E-2	+1.1E-2	+8.7E-5	-1.7E-3	-4.0E-4	-6.3E-4
1	850	+9.5E-3	+1.1E-2	-8.7E-5	-2.7E-3	-2.3E-4	-8.1E-4
2	850	+9.1E-3	+9.2E-3	-5.8E-5	-1.9E-3	-1.4E-4	-6.6E-4
1	900	-	-	-	-3.1E-3	-2.6E-4	-4.3E-4
2	900	+1.0E-2	+9.1E-3	+1.4E-4	-2.1E-3	-8.7E-5	-5.5E-4

* 10 wt% H_3BO_3, 5 wt% metakaolin, 11M H_3PO_4, 4M HNO_3

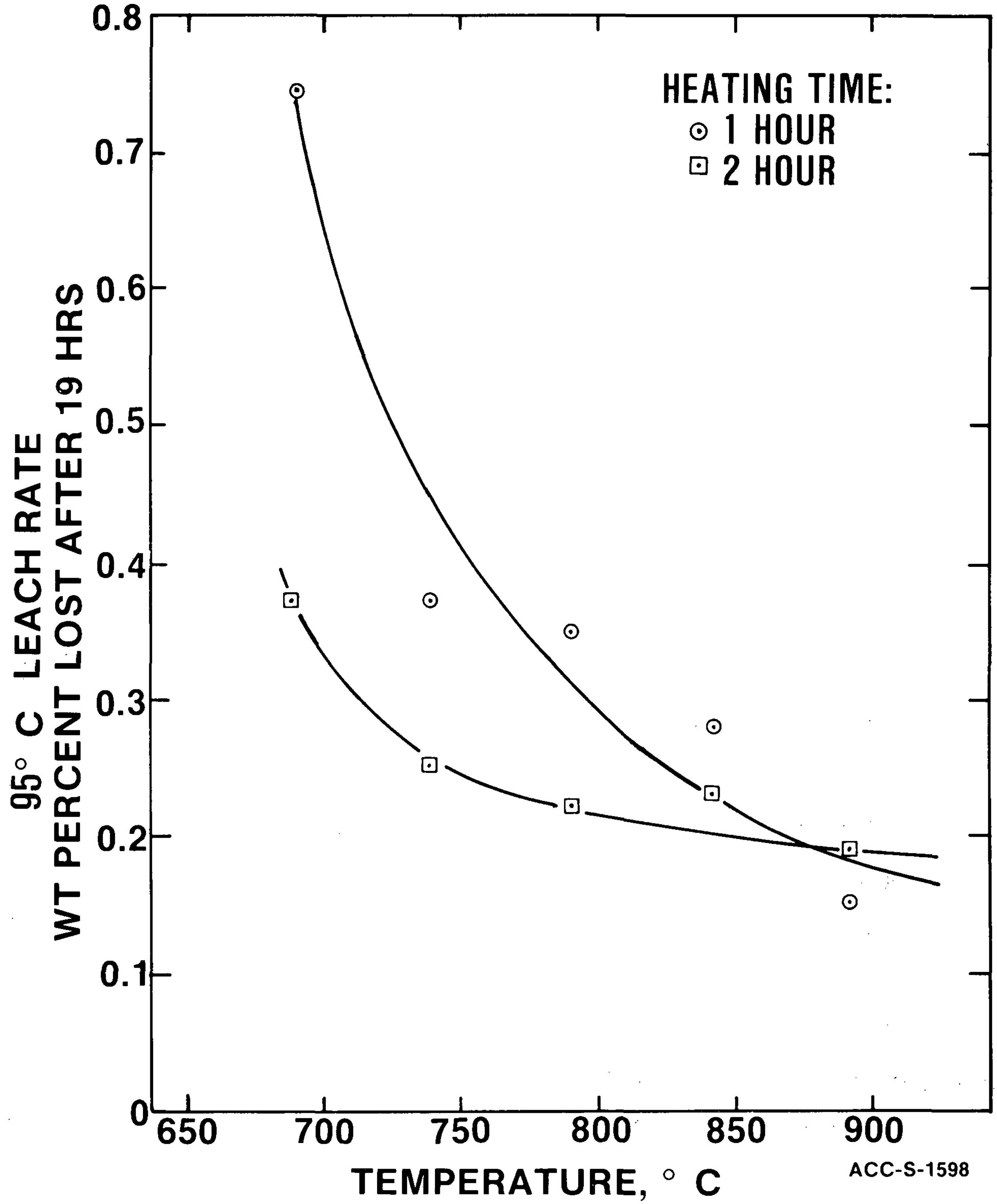

Figure 6. Effect of heat treatment time and temperatures on leach rates of pellets.

Table XV

Brine Solutions used for Pellet Leaching

Ion	Solution "A" (mg/liter) (±3%)	Solution "B" (mg/liter) (± 3%)	Solution "C" (mg/liter) (± 3%)
Na+	42,000	115,000	100
K+	30,000	15	5
Mg++	35,000	10	200
Ca++	600	900	600
Fe+++	2	2	1
Sr++	5	15	15
Li+	20	-	-
Rb+	20	1	1
Cs+	1	1	1
Cl^-	190,000	175,000	200
So_4^{--}	3,500	3,500	1,750
B (BO_3^{---})	1,200	10	-
HCO_3^-	700	10	100
NO_3^-	-	-	20
Br^-	400	400	-
I^-	10	10	-
pH (adjusted)	6.5	6.5	7.5
Specific Gravity	1.2	1.2	1.0

Table XVI

Comparison of Alternatives Waste Forms

Property	Waste Form: Calcine	Pellet	Glass
density g/cc	1.2-1.6	1.1-1.5	2.5-2.75
waste content g/cc	1.2-1.6	0.8-1.3	0.6-1.1
Preparation temp °C	500-550	800-850	1050-1200
Maximum Stable Temp, °C	700	800-850	>550
100 h Soxhlet Leach Resistance $g/cm^2/day$	$<10^{-3}$	10^{-4}-10^{-5}	10^{-5}-10^{-6}
Cs Leach Resistance $g/cm^2/day$ (100 Hr Soxhlet)	$<10^{-1}$	10^{-3}	10^{-4}-10^{-5}

V. Conclusions

Pelletizing high-level ICPP zirconia calcine may be a practical alternative to vitrification or calcine storage. Pelletizing reduces the surface are of calcined waste by a factor of 1000 or more. This greatly reduces dispersibility and improves leach resistance. Reactions between solid and liquid pellet binders and calcine further increase leach resistance of the waste. To date pellets have been made with bulk leach resistance within a factor of 10 of the leach resistance for glass made from the same simulated calcine, however, leach resistance of CS is approximately 10-30 times less.

An integrated pellet pilot plant is being built based upon this pellet development work. The pilot plant will be used to verify a practical process. The pellet pilot plant and development work will form the basis for determining the value of pellets as a waste form for ICPP waste.

VI. Recommendations for Future Work

Variables other than the type and amount of binders affect pellet properties such as leach resistance. To date most pellet development work has focused on binders for producing pellets with zirconia calcine. Two important areas of pelletization need to be investigated further; 1) the effects of calcine particle size on pellet leach resistance, strength, and ability to form pellets, and 2) the effect of heat treatment time and temperature on these properties.

The other types of calcined wastes produced at ICPP will have to be pelletized and the applicability of the pelletizing process to these wastes will have to be studied through the operation of a pelletizing pilot plant and development of binders for the specific calcines.

VIII. References

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10. Code of Federal Regulations, Title 10-Atomic Energy Commission- Part 50, Appendix F.

VII. Appendix

The following tables list the compositions of solid and liquid binders used and leach rates obtained for 34 pellet-forming runs on the 41-cm disc pelletizer for zirconia calcine.

Table I

Leachability of Cs, Sr, and B from Pellets (100 hr Soxhlet at Boiling)

Formulation No.	Solid Binders			Liquid Binders M				Loss wt%	Leach Rate g/cm²/day		
	H_3BO_3	Metakaolin	Bentonite	H_3PO_4	HNO_3	Al_2O_3	% SiO_2		Cs	Sr	Total
P-1	0	0 (10-$Ca(OH)_2$)	0	10	0	0	0	0.31*			
P-2	0	10	0	10	0	0	0	0.50*			
P-3	10	5	0	11	4	0	0	0.80	.148	1.8E-4	8.5E-4
P-4	0	0 (20-$Ca(OH)_2$)	0	11	4	0	0	0.42			
P-5	0	10	(10 $Ca(OH)_2$)	11	0	0	0	no pellets			
P-6	5	5	(5 $Ca(OH)_2$)	11	0	0	0	no pellets			
P-6A	5	5	5	7	4			no pellets			
P-7B	10	0	0	10	0	0	0	1.10	5.0E-2	2.5E-3	3.8E-3
P-7C	10	0	0	10	0			no pellets			
P-8	5	5	0	10	0	0	0	0.84	8.4E-2	1.5E-3	1.8E-3
P-8A	5	5	0	7	4	0	0	0.92	3.8E-3		7.9E-4
P-8B	5	5	0	11	4	0	0	0.96			
P-9								no pellets			
P-11	10	0	0	1	4	0	0	1.40	1.2E-3		
P-12	10	0	0	11	4	0	0	1.40	1.2E-1	7.4E-3	3.4E-5
P-13C	0	20	0	6.5	2	0	0				
P-14								no pellets			
P-15B	10	5	3	7	2	0	0	2.69	1.46E-2	1.85E-3	1.43E-3
P-15C	10	5	3	7	1	2.5	0	1.38	6.0E-3	1.2E-3	1.0E-3
P-16B	10	5	3	7	2	0	0	1.27	6.81E-4	6.64E-4	7.3E-4
P-16C	10	5	3	9	2	0	0	1.53	2.33E-1	1.36E-3	1.9E-4
	10	5	3	9	2	0	0	0.34	7.63E-4	9.70E-4	1.7E-4
P-16D	10	5	3	5	2	0	0	1.92	1.90E-3	1.59E-3	1.2E-3
	10	5	3	5	2	0	0	1.96	2.43E-2	5.07E-4	1.4E-3
P-17A	5	5	5	7	2	0	0	0.70	7.3E-3	2.14E-5	2.9E-4
	5	5	5	7	2	0	0	1.23	4.0E-3	1.1E-5	4.7E-4
P-17B	5	5	5	0	7	2	0	1.21	7.5E-2	5.7E-3	4.9E-4
	5	5	5	0	7	2	0	1.77	4.5E-2	7.2E-3	7.2E-4
P-17C	5	5	5	0	3	0	16	1.36	4.45E-2	1.66E-3	4.0E-4
	5	5	5	0	3	0	16	1.96	4.1E-2	1.4E-3	4.8E-4
P-18A	5	0	5	7	2	0	0	1.11	1.7E-2	2.0E-2	2.7E-4
P-18B	5	0	5	9	2	0	0	1.17	4.7E-2	2.7E-4	5.0E-4
P-18C	5	0	5	3	0	0	16	1.54	1.06E-1	1.78E-3	5.9E-4
P-18D	5	0	5	6	0	1	0	1.02	4.06E-2	6.09E-4	2.1E-4
P-19A	0	5	5	7	2	0	0	1.12	6.52E-3	1.44E-3	5.0E-4
P-19B	0	5	5	7	4	0	0	1.03	9.5E-3	1.1E-4	3.5E-4
P-19C	0	5	5	7	1	0	0	1.54	2.9E-3	1.4E-4	3.0E-4
P-19D	0	5	5	7	0	0	0	1.22	7.7E-3	4.0E-4	6.8E-4