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INTERIM REPORT ON CONCRETED URANIUM FINES
AND CHIPS BILLET CURING TESTS - A BASIS
FOR RESUMING SHIPMENT OF CONCRETED
URANIUM SCRAP BILLETS

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Subject Index

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7. NF Brewer, RMI		30. JP Schmidt	100-N		
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INTERIM REPORT ON CONCRETED URANIUM FINES AND CHIPS BILLET CURING TESTS - A BASIS FOR RESUMING SHIPMENTS OF CONCRETED URANIUM SCRAP BILLETS

INTRODUCTION

In 1971 UNC[†] (DUN[§] at that time) converted the form of return shipments of uranium lathe turnings and saw fines. Up to 1971, the turnings and fines were oxidized (burned). Environmental concerns associated with the uranium scrap burner resulted in development of a process for encapsulating the metallic uranium turnings and fines in concrete.¹ Experiments conducted at that time indicated that the concretion process was safe and it was used without incident until August 1977 when six concreted billets burned when at least one billet autoignited (see photograph in Figure 1). Concreted billets are cast into thin sheet metal cans, about 0.010-inch thick (0.2 mm), with a capacity of 0.97 cubic feet (27 liters). The heat of hydration combined with the warm August temperatures of up to 34C (93F) in a non-airconditioned metal building (304 Building) were established as the cause. The solar heat load was calculated to raise the average room temperature to 53C (128F) (see Appendix A) and with a heat of hydration of about 14C (26F) would have produced about 68C (154F) maximum temperature within the non-cured billets. The fire alarm was not tripped and no flame or smoke was generated since there were no other flammable materials present. The requirement to cold water spray the billets during the initial curing period was instituted as a result of this incident.²

In July, 1979, a second incident occurred, this time in the 3712 Building warehouse.³ The rapid oxidation of the uranium caused sufficient heat to ignite the wooden shipping boxes, destroying or damaging a total of 21 concreted billets. Again, warm summer weather of up to 43C (110F) was being experienced, which was calculated to raise the average room temperature to about 56C (132F). It is presumed that the billets had been boxed for shipment before they were fully cured and it was concluded that the enclosed box space plus high room temperatures retained the heat of hydration and heat of oxidation sufficiently to cause auto-ignition of one or more billets.

Due to the seriousness of the warehouse fire and the obvious potential for an in-shipment fire, all concretion and shipping of uranium chips and fines billets were suspended until the causes of the fire were defined and corrected.³

[†] UNC Nuclear Industries.

[§] Douglas United Nuclear, Inc.

Introduction (continued)

DOE-RL[†] requested UNC to perform a safety evaluation of the packaging and shipping operations prior to resuming activities. Alternatives to the concretion process were to be identified. DOE-RL approval was also required prior to resuming shipments.⁴

A series of tests were conducted to primarily:

1. Determine what the autoignition temperature is for various curing conditions.
2. Determine the conditions necessary to assure that concreted billets of uranium fines and chips are sufficiently cured for offsite shipment.

The 303-K Building was modified to serve as a controlled test room. Air sampling, hydrogen monitoring and temperature recording equipment were installed. An externally controlled heating system was added to the room. Concreted billet autoignition tests were initiated on September 19, 1979.

SUMMARY

Through extensive testing and analyses of the concretion process, billets and shipping conditions, it has been determined that properly cured concreted billets can be safely shipped to National Lead Company of Ohio (NLO), Fernald, Ohio. During curing, billets will be dried for 26 days prior to shipment with the last 10 days between 54-66C (130-150F). Such dried billets can withstand temperatures up to 85C (185F). The maximum billet temperature that can be expected to occur in shipment is 50C (123F). Thus, the drying cycle becomes a "burning test" at temperatures which the billets will not reach during shipment to NLO.

DISCUSSION

Test results show (see Appendix B) that when uranium fines and chips are uniformly mixed with masonry cement, properly cooled and cured, and heated to drive off excess water, the concreted uranium can be safely shipped to Ohio without any potential fire hazard as a result of the concretion process.

When a stationary trailer load of concreted billets is exposed to sunlight, the external surface of the trailer will absorb heat from the sun. However, the boxed billets within a trailer could never reach the external trailer surface temperature due to the cyclic nature of solar heating, the heat transfer into the trailer, and the heat absorption due to the specific heat of the contents within the trailer.

[†] Dept. of Energy - Richland Operations Office.

Discussion (continued)

Actual experimental data described below confirm this conclusion. With the large vertical side area of a trailer facing south, more heat will be absorbed during December than during June since the side is more normal to the sun in December. (The total heat absorption of the trailer is relatively independent of the ambient temperature but is dependent primarily on the angle the sun strikes the surface, the cloud cover and atmospheric dust content.)

To test the above theories, temperature tests were run for over 32 days on one of the aluminum sided trailers (see photograph in Figure 2) used for shipping concreted billets with thermocouples placed at the following locations.

1. Ambient air in the shade.
2. Exterior trailer surface on south side about 1 1/2 feet below top (surface is covered with road grime).
3. Interior air at three locations; one foot below ceiling, middle and one foot above floor (shipping box location).
4. Exterior surface of two concreted billets within a standard wooden shipping box (NLO No. G-4292⁵).

The largest ΔT observed between the maximum ambient air temperature and the exterior trailer surface, interior air one foot above the floor, and billet surface was 37C (67F), 15C (27F) and 2C (4F), respectively. See Figure 3 for typical temperature recording over a two day period. See Figure 4 for the relationships of the largest ΔT between the maximum ambient air temperature and 1) the maximum exterior trailer surface temperature on the south side, 2) the maximum trailer interior air temperature one foot above the floor and 3) the maximum boxed billet surface temperature.

The particle size of saw fines and lathe chips is a contributing factor to autoignition of concreted billets. With pyrophoric metals, such as uranium and zirconium the finer the particle size the more easily the material will autoignite. Thus, the uranium and zirconium bearing saw fines from the coextrusion cut-up saws will be more reactive than the uranium and zirconium lathe chips from the counterbore operation. The saw fines contain about 60 to 70% U and about 4.5% Zr while the lathe chips contain about 96% U and 2.8% Zr. Uranium fines are more pyrophoric than zirconium fines. Kopelman and Compton⁶ state that "uranium is so much more reactive than zirconium that, whereas zirconium powder is usually stored under water, uranium powder of the same particle size will catch fire under boiling water".

Discussion (continued)

Uranium bearing fines must be adequately mixed with the wet cement to prevent relatively low autoignition temperatures. A test was run in which about two pounds of unmixed fines were placed in two billet cans during casting of a mixture of fines and chips. After water sprinkling for three days to remove some of the heat of hydration, the two concreted billets were placed in a warm room up to 63C (145F) and, after 37 hours, one of the billets autoignited.

The release of hydrogen as billet temperatures increase to autoignition indicates that an aqueous reaction ($U + 2H_2O \rightarrow UO_2 + 2H_2$) is the key source of heat generation. Since there is an excess of "free" water in concrete over that required for hydration and hydrolysis, long term drying tests for 26 days (after initial cooling to remove the heat of hydration) in a warm atmosphere up to 66C (150F) was found to be effective in removing this excess water. This drying method produced billets that can withstand 85C (185F).

The highest recorded temperature along the shipping routes as shown in Figure 5 was 48C (119F) at Pendleton, Oregon in 1898. Since the largest ΔT observed between the ambient air temperature and the boxed billet surface temperature within a trailer is 2C (4F), any billets cured for 26 days above 50C (123F) will be able to withstand the highest recorded ambient shipping temperature.

RECOMMENDATIONS

A. Disposal of Current Inventories

Due to a high fire hazard, fines and chips must be stored outside in 30-gallon water filled drums with a diked area having good drainage to the process sewer and with a water sprinkling system for use during warm weather. The only properly equipped storage area holds 49 drums. A temporary storage area has been set up in a non-optimum area to hold the remaining drums and there is now a total of 145 drums. (See photograph of storage area in Figure 6.) It is recommended that chips and fines be concreted as soon as possible since the concreted billets can be stored safer than the 30-gallon drums of chips and fines.

It is also recommended that the inventory of chips and fines and burned concrete billet debris be concreted as per Specification X-506 and Operating Procedure 4-SP-534 with the following restrictions:

1. The burned debris will be mixed with chopped[†] chips at one drum of debris to one drum of chips. Otherwise, the burned debris that is reconcreted may not burn properly during the recovery process at NLO.
2. The water content of the wet cement will be controlled to less than 0.6 lb of water per 1.0 lb of dry cement. This would be a maximum of 20 quarts (19 liters) of water per 70 lb bag of masonry cement.
3. Cool the newly poured billets in "cooling pans" which contain about eight inches of running water for a minimum of seven days to remove the heat of hydration. Place a lid on the freshly poured billet but remove the lid as soon as possible after solidification to allow for moisture removal during the cooling and curing process.
4. Transfer cooled billets to the warm 303-K Building and let cure for at least 26 days without lids. The warm room will be maintained in the 50-66C (123-150F) range with the last ten days above 54C (130F).
5. Transfer cured billets to a work area and let cool for at least three days to stabilize the billet temperature before infrared scanning to detect any billets with abnormal temperatures. Load billets in boxes for shipment.
6. Audits and checklists will be performed to assure that the concretion process procedures are in compliance.

If the shipping of concreted billets is not resumed shortly, there will be a serious problem with inventories of fines, chips and/or concreted billets.

[†] All of the long, springy lathe chips are passed through a chip chopper or shredder to make the chips more compactable.

Recommendations (continued)

B. Short Range Tests

1. Improve Mixer

It was noted that in the conventional cement mixer (see photograph in Figure 7) used in the 304 Building the uranium fines would settle to the base of the mixer and not mix properly with the wet cement and chips. A plaster type mixer which has rotating paddles in a horizontal cylindrical body has been modified for mixing chips (see photograph in Figure 8). This mixer was satisfactorily tested in the 313 Building using stainless steel and Cu-Si chopped chips and will be used for mixing uranium chips and fines when the concretion process resumes operation.

2. Reduced Water Content

Tests using smaller than normal water-to-dry cement ratios will be conducted to determine if satisfactory low "free" water concrete can be produced. The normal water content has been 0.55 lb of water per 1.0 lb of dry cement. Less water content may be possible using the plaster type mixer.

3. Oven Tests

When the production of concreted billets resumes as per the process described above in Recommendations, A, production billets will be subjected to oven tests up to 93C (200F).

C. Long Range Alternatives to the Concretion Process

Since the value of the uranium in the lathe chips and saw fines averages over \$500,000 per year, it is imperative that the uranium be returned to the feed site for recovery. The alternatives to the concretion process for preparing the uranium fines and chips for shipment are 1) a scrap burner to produce uranium oxides, 2) chemical conversion to a stable uranium salt and 3) water autoclave conversion to uranium oxides. These alternatives are all long range items and require substantial monies for equipment (\$50,000 to \$310,000) and process development; whereas, the concretion process is operable and needs only minor refinements. The environmental problems to control the hot air-borne uranium oxides, NO₂ gas or hydrogen gas from the alternate processes would have to be overcome.

Figure 1.
Appearance of First Concreted Uranium Billets
to Autoignite, August 1977.

Figure 2.

Appearance of Aluminum Sided Trailer Used for Temperature Tests.
Note Yellow Colored Thermocouple Wire Positioned on South
Side to About $1\frac{1}{2}$ Feet Below Top.

FIGURE 3.

RELATIONSHIP OF AMBIENT AIR TEMPERATURE WITH BILLET AND TRAILER TEMPERATURE

FIGURE 4.

AMBIENT AIR TEMPERATURE VERSUS MAXIMUM TEMPERATURE DIFFERENCE BETWEEN BILLET AND TRAILER

Figure 5.

Truck-trailer Routes from Hanford, WA to Fernald, OH for Shipment
of Concreted Billets with Highest Recorded Temperature at
Principle Cities Along the Routes.^{9, 10}

Figure 6.
Outside Storage Location of Water-filled Drums of Uranium Fines and Turnings.
Array in Foreground is Only Properly Equipped Storage Area.
Drums are Spaced Apart to Prevent Fire Propagation.

Figure 7.

Conventional Type Cement Mixer Used for Concreting Uranium Fines and Turnings.

Figure 8.
Modified Plaster Type Mixer to be Used When the Concretion Process Resumes Operation.

APPENDIX ASOLAR HEATING CALCULATIONS

When an object (building, trailer, etc.) is placed in direct sunlight, the object will absorb solar heat. Excess heat will then be transferred from the surface by radiation and by natural convection to the environment until a steady-state relation exists.¹¹

$$Q_s = Q_c + Q_r = \alpha q A_s = \text{total heat flow} \quad (\text{equation 1})$$

$$\alpha q A_s = 0.19 A_c (T_s - T_a)^{4/3} + 0.173 \epsilon A_r \{ [T_s + 460]/100 \}^4 - [T_a + 460]/100 \}^4 \quad (\text{equation 2})$$

Where:

- Q_s = solar heat load
- Q_c = convection heat flow
- Q_r = radiative heat flow
- q = solar incident heating value
- α = solar absorptivity
- A_s = area exposed to sun
- $A_c = A_r$ = area of heat transfer
- ϵ = emissivity of surface
- T_a = ambient temperature
- T_s = surface temperature

The rate at which the earth intercepts solar energy on a surface normal to the sun's rays at a point above the earth's atmosphere is 442 Btu/hr-ft², or 10,600 BTU/ft²- day; this value, known as the solar constant, increases (decreases) by 3.5% in December (June). The amount of solar radiation received at a point on the surface of the earth on a clear day when the sun is at the zenith varies, but 70% of the solar constant value is generally considered to be sufficiently accurate for engineering purposes.¹¹

Figure A-1 gives the relative total daily radiation incident on a horizontal or south-facing vertical surface as a function of latitude. Multiplication of the appropriate values from Figure A-1 by the 24 hour solar constant (10,600 Btu/ft²- day) and the local mass transmittance of the earth's atmosphere (~ 0.7) gives the daily incidence on a vertical or horizontal surface.¹²

Scattered radiation which is small, is not included. (The 300 Area is at about latitude 46.4°N , and Fernald, Ohio is at about latitude 39.3°N .) To determine the heat load affecting a given surface, the daily incident heating value must be multiplied by the absorptivity, α , of that surface.

Values of the solar heat load can be calculated for each surface of the object (e.g., horizontal top, vertical south side, vertical east side and vertical west side) and the sum of these values yields the total solar heat load, Q_s .

After determining the total heat load, Q_s , equation 2 can be solved via an iterative process at various ambient temperatures, T_a , to determine the surface temperature T_s .

Using this procedure, the surface temperature, $^{\circ}\text{F}$, and average heat load (Btu/hr ft^2) was calculated for the hottest day in the 304 and 3712 Buildings [34°C (93°F) and 43°C (110°F), respectively] when the concretion billet fires occurred in 1977 and 1979. Then assuming the ceiling and heated metal walls act like radiant heaters, an average room temperature was estimated as per Figure 12 in Reference 13. An $\alpha = 0.89$ and an $\epsilon = 0.28$ was used.¹¹ The estimated average room temperature for the 304 Building was calculated at 53°C (128°F) and for the 3712 Building was 56°C (132°F).

Equation 2 was also used to calculate the surface temperature on the south facing vertical side of a dirty aluminum bodied trailer (see photograph in Figure 2) to compare this temperature with actual recorded temperatures. An $\alpha = 0.9$ and $\epsilon = 0.2$ was used during the equinox. The results from Equation 2 compares quite closely with maximum observed temperature measurements (see Figure A-2). For example, at an ambient air temperature of 16°C (60°F) the calculated surface temperature was 50°C (123°F) and the recorded maximum surface temperature was 53°C (127°F).

FIGURE A-1.

**RELATIVE TOTAL DAILY SOLAR RADIATION INCIDENT
ON A HORIZONTAL OR SOUTH-FACING VERTICAL
SURFACE AS A FUNCTION OF LATITUDE¹²**

FIGURE A-2.

OUTER SURFACE TEMPERATURE ON SOUTH SIDE OF TRAILER

DETAILED TEST DESCRIPTION AND RESULTSA. Equipment and Facilities

The concrete test billets mentioned in this report were made using the scale, chip chopper and cement mixer previously used for routine billet production in the 304 Building. Thermocouples were placed in the center of most of the new test billets and near the bottom and the center of a few of the billets. (There was an insignificant difference in temperature between the center and bottom of a billet during autoignition.)

The decontamination room in the 303-K Building was prepared for heat testing the concreted billets. All electricity to the room was disconnected and the blower for the steam space heater was powered by an air motor. The maximum temperature obtainable in the room varied with the outside temperature and ranged from 64C (147F) down to 46C (115F). All burnable materials and unneeded equipment were removed. To reduce the chance for contamination to the surroundings all wall penetrations were sealed. After the second test, which resulted in 3 burned billets, an exhaust blower with a HEPA filter was installed on the roof vent to bleed off excess hydrogen without contaminating the roof. The concreted billets were placed in pans to minimize contamination spread and make it easier to shovel the burned billets into water filled barrels during clean-up.

Two steam heated ovens were fabricated and installed in the 303-K Building for testing up to about 100C (212F). A hydrogen gas detector was installed which tripped an alarm light above the building at about 0.8% hydrogen (4% hydrogen is the low explosive value). The highest hydrogen value obtained during any test was 1% before the vent was opened or the exhaust blower was turned on.

Billet temperatures during cooling in the 304 Building and during heating in the 303-K Building were recorded every 30 minutes on a Fluke Model 2240B data logger with 20 channels. The room temperatures and oven temperatures were also recorded.

B. Types of Billets Tested

The concrete billets prepared for this portion of the this program had a constant ratio of water to dry masonry cement of 0.55 lb of water to 1.0 lb of cement. Masonry cement has the approximate chemical composition as follows:

Appendix B

B. Types of Billets Tested (continued)

47% Limestone (CaCO_3)

3% Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)

50% Portland Cement, Type II:

- 43% $3\text{CaO} \cdot \text{SiO}_2$
- 30% $2\text{CaO} \cdot \text{SiO}_2$
- 13% $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$
- 6% $3\text{CaO} \cdot \text{Al}_2\text{O}_3$
- 3% CaSO_4
- 3% MgO

With the addition of water, the cement hardens primarily by hydration and with some hydrolysis.

The following types of test billets were prepared during this study (see Table I for brief description of referenced test number):

1. Fines and chips billets:

- a. An average ratio of 0.37 lb of moist fines to 1.0 lb of moist single chopped chips with about 40 lb of uranium per billet. (Used in Test Nos. I-1, I-2, II-1 and III-1.)
- b. A heavy ratio of 1.6 lbs of moist fines to 1.0 lb of moist single chopped chips with about 64 lb of uranium per billet. (Used in Test Nos. I-3, I-4, II-2, II-3, II-4, and III-2.)

2. Chips only billets:

- a. Single chopped chips (as normally done) which have a volume reduction of 2 1/3:1 over unchopped chips with about 27 lb of uranium per billet. (Used in Test Nos. IV-1, VI-2, and VI-4.)
- b. Double chopped chips which have a volume reduction ratio of 4:1 over unchopped chips with about 34 lb of uranium per billet. (Used in Test Nos. IV-2, VI-1, VI-3, and VI-4.)

3. Heavy uranium fines to chips ratio billets with about 2 lbs of unmixed fines:

- a. Unmixed fines in the center of the billet. (Used in Test No. II-4.)
- b. Unmixed fines at the bottom of the billet. (Used in Test No. II-3.)

4. Cement only billets to determine the heat of hydration.

Several "long cured" production billets that were cast in April or May, 1979, and have been in storage since that time were also tested. (Used in Test Nos. V, VII, and VIII.)

C. Test Conditions

Several different curing methods were investigated:

1. Sprinkle billets with cold water for at least seven days. (Test Nos. III-1, III-2, IV-1, and IV-2.)
2. Place non-sprinkled fines and chips billets in a non-airconditioned building, at about 39C (102F) for five days and then raise the temperature to 63C (145F). (Test No. I-1 and I-3.)
3. Wrap the fines and chips billet in asbestos cloth insulation and cover with a 55-gallon drum with the same temperature conditions as in item 2. (Test Nos. I-2 and I-4.)
4. Sprinkle billets for at least seven days and then place in a 93C (200F) oven. (Test Nos. III-1, III-2, IV-1 and IV-2.)
5. Sprinkle fines and chips billets for at least three days then insulate as in item 3, and place in 63C (145F) atmosphere. (Test Nos. II-1 and II-2.)
6. Sprinkle the fines and chips billets containing unmixed fines for three days and then place in 63C (145F) atmosphere. (Test Nos. II-3 and II-4.)
7. Sprinkle the chips only billets for seven days and then place in about 58C (136F) atmosphere:
 - a. After eight days in warm atmosphere place billets in 97C (207F) oven. (Test Nos. VI-1 and VI-2.)
 - b. After 40 days in warm atmosphere with last 32 days with lids off, place billets in 85C (185F) oven for ten days then raise temperature to 93C (200F). (Test No. VI-3.)
8. Test "long cured" production billets from April or May, 1979:
 - a. Place in about 58C (136F) atmosphere. (Tests VII and VIII.)
 - b. Place in about 95C (203F) oven. (Test No. V.)
 - c. After 22 days in warm atmosphere with lids off for last 14 days, place in 85C (185F) oven. (Test VII-1.)
 - d. After 40 days in warm atmosphere with lids off for last 32 days, place in 85C (185F) oven. (Test VII-2.)
 - e. After 82 days in warm atmosphere with lids off for last 74 days, place in 85C (185F) oven. (Test VIII-1.)
 - f. After eight days in warm atmosphere with lids off, place in 85C (185F) oven. (Test VIII-2.)

D. Test Results

1. Heat of Hydration

The maximum heat of hydration is reached at the center of the billets in about 10-15 hours after casting.

As shown in Figure B-1 the cement only billet had the highest heat of hydration followed by the average fines to chips ratio billet and heavy fines to chips ratio billet. This effect is probably due to (1) the increased amount of uranium improving the heat transfer, (2) the heat capacity of the uranium which would absorb some of the heat of hydration and (3) less volume of cement.

The effectiveness of cold water sprinkling on reducing the heat of hydration is shown in Figure B-2.

2. Non-cooled Billet Tests (Test Nos. I-1, I-2, I-3, and I-4.)

One of the eight fines and chips billets that had been placed in the warm building at 35-39C (95-102F) autoignited. The heavy uranium fines to chips ratio billet autoignited after about three days at the higher temperature (a total of 214 hours after pouring) and reached a maximum temperature of 646C (1195F) at the center of the billet. (See photograph in Figure B-3.)

It was found that the seven unburned billets containing fines and chips had split the steel can at the seam and the concreted billets were cracked, some so badly that you could see halfway through the billet and with pieces of lathe chips extending out into the open crack. The unburned but damaged billets included heavy and average fines to chips ratio billets and insulated and uninsulated billets.

3. Fire Simulation Tests (Test Nos. II-1, II-2, II-3, and II-4.)

To simulate the proposed cause of the 3712 Building fire, average and heavy fines to chips ratio billets were sprinkled for three days then insulated with asbestos cloth and a 55-gallon drum placed upside down over the billet before being placed in the 63C (145F) room. A heavy fines to chips ratio billet with about two lbs of unmixed fines placed in the center and a similar billet with about two lbs of unmixed fines placed in the bottom of the billet were sprinkled for three days and placed in the 63C (145F) room.

3. Fire Simulation Tests (continued)

The billet with the unmixed fines in the center autoignited 37 hours after being placed in the warm room (108 hours after being poured) and reached a temperature of 803C (1477F). (See temperature curve in Figure B-4.) The other billet with unmixed fines in the bottom of the billet did not autoignite although it was badly cracked and reached a temperature of 73C (153F). (See photograph in Figure B-5.) Both billets had thermocouples at the center.

4. Warm Room Drying Tests (Test Nos. VI, VII, VIII.)

The release of hydrogen as the billet temperature increases to an autoignition temperature indicates that an aqueous reaction ($U + 2H_2O \rightarrow UO_2 + 2H_2$) is the key source of heat generation. Since there is an excess of "free" water in concrete over that required for hydration and hydrolysis, long term curing (after cooling) in a warm atmosphere was tested prior to subjecting billets to oven tests.

a. In October, six double chopped and six single chopped chips only billets and six "long cured" production billets were placed in the warm 303-K Building atmosphere to determine if they would autoignite at about 58C (136F). (Test Nos. VI, VII and VIII-1.) After eight days there were no noticeable reaction, so the can lids were removed to allow moisture to escape, except for the two billets placed in the ovens. (Test Nos. VI-1 and VI-2.) Nine of the chips only and three of the "long cured" billets remained in the warm atmosphere for 82 days with no noticeable reaction. (Test Nos. VI-4 and VII-3.) The remaining four billets were used in oven tests. (Test Nos. VI-3, VII-1 and VII-2.)

b. In March 1980, all of the 0.95% U^{235} concreted uranium billets in storage (297 total) were placed in the 303-K for long term drying (over 28 days) with the lids removed at temperatures between 53C and 61C (127-142F). This included 97 unburned billets from the autoignition tests and 200 "long cured" production billets in storage. After eight days, two of the "long cured" billets were used in an oven test (test No. VIII-2). None of the billets were damaged by this long term drying process.

5. Oven Tests:

a. Oven Temperature at about 85C (185F):

1. Two "long cured" billets that were (a) poured in April or May, 1979, and (b) placed in a warm 55-58C (131-136F) atmosphere for 22 days and with the lid removed for the last 14 days, were placed in the heated oven. (Test No. VII-1.)

5. Oven Tests (continued)

a. Oven temperature at about 85C (185F) (continued)

Autoignition occurred 52 and 120 hours after being placed in the oven and reached a maximum temperature of 244C (471F) and 360C (680F), respectively, at the top surface of the billets.

These two billets had unusual temperature curves since there was no plateau at about 95C (203F) and the autoignition occurred later than any of the other oven tests which varied between 27 and 47 hours. This difference in temperature curves and autoignition times may be due to less "free" water in the billets.

2. After 240 hours in the 80-90C (176-194F) oven, a double chopped chips only billet (Test No. VI-3) and a "long cured" billet poured last April or May (Test VII-2) showed no signs of autoignition. Both billets had been in the warm 55-58C (131-136F) atmosphere for 40 days with the last 32 days with the lids off. The oven temperature was then increased to about 93C (200F) as noted below in b.5).
3. In March, two of the "long cured" billets that had been dried for 82 days (see above in 4.a.) were placed in the oven (Test No. VIII-1). One billet for 105 hours at 84-93C (183-199F) and the other for 187 hours at 80-89C (176-192F). No autoignition occurred and the cans were not split.
4. After eight days of drying in the warm room (Test No. VIII-2), two "long cure" billets were placed in the drum ovens at 82-88C (180-190F). One billet autoignited after 162 hours in the oven. The other billet did not burn after 19 days in the oven and the can did not split.

b. Oven Temperatures at about 93C (200F)

Only one of the various types of concreted billets tested to-date could withstand exposure to 93C (200F). This included the following tests:

1. Heavy and average fines to chips ratio billets that had been sprinkled for 19 days and then placed in the oven. (Tests Nos. III-1 and III-2.) The average fines to chips ratio billet autoignited after 27 hours in the oven and reached 446C (834F) (see temperature curve in Figure B-6). The heavy fines to chips ratio billet autoignited after 32 hours in the oven reached 314C (597F). Thermocouples were at the center of the billets.

5. Oven Tests (continued)

b. Oven Temperatures at about 93C (continued)

The temperature curve shown in Figure B-6 is typical of most of the burned billets. A plateau usually occurs for several hours at about 95C (203F) before rising exponentially at autoignition.

2. Double and single chopped chips only billets that had been sprinkled for seven days and then placed in the oven. (Test Nos. IV-1 and IV-2.) The double chopped chips billet autoignited 43 hours after being placed in the heated drum and reached 430C (806F) before cooling down. The steel can was still intact and the top surface of the concrete was not noticeably cracked. The single chopped chips billet autoignited after 47 hours and reached a maximum temperature of 157C (316F) before cooling down. Both billets had thermocouples at the billet center.
3. Two "long cured" billets which were poured in April or May, 1979, and have been in storage since that time were placed in the heated drum ovens at about 95C (203F). (Test No. V.) The billets autoignited after 33 and 39 hours and reached a maximum temperature of 334C (633F) and 388C (730F), respectively, at the top surface of the billets. The latter billet can did not split open although the can was badly discolored and the paper tags charred.
4. Double and single chips only concreted billets autoignited 30 and 42 hours, respectively, after being placed in heated drum ovens at 95C (203F). (Test Nos. VI-1 and VI-2.) Both billets had been sprinkled for seven days and then subjected for eight days to the warm 58C (136F) 303-K Building atmosphere with lids in place. The maximum temperature reached for the double chopped billets was 483C (900F) and for the single chopped billet 244C (471F) at the center of the billets. The former billet can was only slightly split open.
5. The double chopped chips only billet and the "long cured" billet that had been dried for 32 days with the can lid off and subjected to about 85C (185F) for 240 hours (see above in 5.a.2) were then subjected to a 93C (200F) oven test. The "long cured" billet (Test No. VII-2) autoignited after 93 hours at the 93C (200F) temperature and reached a maximum temperature of 222C (432F) at the surface of the billet. There was no noticeable hydrogen release on the hydrogen indicator which may indicate that there was very little "free" water to react with the uranium.

5. Oven Tests (continued)

b. Oven Temperatures at about 93 C (continued)

The chips only billet (Test No. VI-3) was at the high oven temperature for over 790 hours before the test was terminated and showed no signs of autoignition. The can did not split and the billet did not even crack as shown in the photograph in Figure B-7. This billet should be more resistant to oxidation since it contains no uranium fines which are known to be more pyrophoric than chips.

E. The Concrete Uranium Scrap Billet Ignition Process

The testing has led to an increased understanding of the ignition process leading to the August, 1977 and July, 1979 fires involving concreted uranium scrap billets. Since greater than 10,000 billets have been processed and shipped since 1971, and only two fires have occurred, conditions for ignition are obviously borderline. This point is presented to put the information into perspective only, not to suggest that a low probability of ignition is acceptable.

Three separate heat sources appear to play distinct roles in the ignition process. They are:

1. The ambient temperature.
2. The exothermic hydration process associated with the curing of cement.
3. The exothermic reaction involving the oxidation of uranium with water; the oxidation of saw fines involving a high surface to volume ratio being more important than the oxidation of chips with relatively low surface to volume ratio.

Since the fires experienced have occurred in the high ambient temperature months, experience supports logic that ambient temperature is the basic trigger mechanism. When ambient temperatures are high, the cement hydration process occurs at relatively high rates. Being an exothermic reaction, the rate at which hydration proceeds is a factor on temperatures reached within the billet during curing. Test data shows that a higher ambient temperature during curing does lead to higher ΔT 's between the ambient temperature and the internal billet temperature. (Compare heat of hydration curves in Figures B-1 and B-2.)

E. The Concrete Uranium Scrap Billet Ignition Process (continued)

The final heat source whose contribution is necessary for ignition is oxidation of the uranium by "free" water in the billet. When the ambient temperature is high and, as a result the hydration rate is high, internal billet temperatures are such that uranium oxidation proceeds at a rate sufficient to further elevate the internal billet temperatures. During July, 1977, and August, 1979, conditions were sufficient in at least two concreted scrap billets to raise internal temperature to the point the uranium autoignited.

The actual ignition temperature is a variable. It depends on the total weight of uranium in a billet, the percentage of this uranium that is in the form of fines, the amount of water used in mixing the cement, the amount of "free" water in the cured billet, and the curing conditions, i.e., is the billet can lid on or off, are the billets cooled initially, curing time and temperature, etc.

The amount of "free" water in billets cured with the lids sealed is significant. For example, when the "long cured" production billets were dried this spring for over 28 days between 53 and 61C (127 and 142F), the average loss per billet was as follows:

<u>Casting Date</u>	<u>No. of Billets</u>	<u>Average Water Loss/Billet</u>	
		<u>Weight</u>	<u>Volume</u>
April and May, 1979	75	1.7 lb (0.8Kg)	0.8 qt (0.9 liter)
June, 1979	73	2.2 lb (1.0Kg)	1.1 qt (1.2 liter)
July, 1979	52	5.3 lb (2.4Kg)	2.5 qt (2.9 liter)

The variation in water loss per billet is probably a combination of the differences in the uncontrolled amount of water used in mixing the concrete and the longer time for the cement to react chemcially with the water by hydration and hydrolysis.

The proposed mixing, cooling and drying process for future concretion billets, is expected to result in dried billets with insignificant "free" water content. Also, the drying temperature of 54-66C (130-160F) will be greater than the maximum possible temperature of 50C (123F) that the billets are expected to be exposed to during shipping. Tests have indicated that such dried billets can withstand long exposures to temperatures on the order of 85C (185F) which is much higher than the maximum possible shipping temperature.

TABLE I

SUMMARY OF WARM ROOM AND OVEN BILLET AUTOIGNITION TESTS

<u>Test No.</u>	<u>Number and Type of Billets</u>	<u>Treatment</u>	<u>Results</u>
I-1	2-average fines - to - chips ratio. Air cured.	Not sprinkled. Placed in warm room at ~ 39C for five days then raised to ~ 63C for three days.	Cans split. Did not burn. Billets had small cracks.
I-2	2-average fines-to-chips ratio. Insulated during curing.	Not sprinkled. Placed in warm room at ~ 39C for five days then raised to ~ 63C for three days.	Cans split. Did not burn. Billets had moderate cracks.
I-3	2-heavy fines-to-chips ratio. Air cured.	Not sprinkled. Placed in warm room at ~ 39C for five days then raised to ~ 63C for three days.	One billet burned after 76 hours in the ~ 63C room reaching 646C. Other billet badly cracked and split open but did not burn.
I-4	2-heavy fines-to-chips ratio. Insulated during curing.	Not sprinkled. Placed in warm room at ~ 39C for five days then raised to ~ 63C for three days.	Cans badly split. Did not burn. Billets badly cracked.
II-1	2-average fines-to-chips ratio.	Sprinkled three days. Placed in warm room at ~ 63C for two days. Insulated during curing.	Did not burn. Can not split. Billet still good.
II-2	2-heavy fines-to-chips ratio.	Sprinkled three days. Placed in warm room at ~ 63C for two days. Insulated during curing.	Did not burn. Cans split open. Billets moderately cracked.
II-3	1-heavy fines-to-chips ratio with ~ 2 lbs unmixed fines in bottom of can.	Sprinkled three days. Placed in warm room at ~ 63C for two days.	Did not burn. Can split open. Billet badly cracked.
II-4	1-heavy fines-to-chips ratio with ~ 2 lbs unmixed fines in middle of billet.	Sprinkled three days. Placed in warm room at ~ 63C for two days.	Billet burned after 37 hours in the ~ 63C room reaching 803C.
III-1	1-average fines-to-chips ratio.	Sprinkled 19 days then placed in oven at ~ 97C.	Billet burned after ~ 27 hours in the oven reaching 446C.
III-2	1-heavy fines-to-chips ratio.	Sprinkled 19 days then placed in oven at ~ 97C.	Billet burned after ~ 32 hours in the oven reaching 314C.

Table I

B-11

UNI-1454

<u>Test No.</u>	<u>Number and Type of Billets</u>	<u>Treatment</u>	<u>Results</u>
IV-1	1-single chopped chips.	Sprinkled seven days then placed in oven at ~97C.	Billet burned after 47 hours in the oven reaching only 157C.
IV-2	1-double chopped chips.	Sprinkled seven days then placed in oven at 97C.	Billet burned after 43 hours in the oven reaching 430C. Can did not split.
V	2-fines and chips production billets cast in April or May, 1979.	Placed in oven at 95C.	Both billets burned after 32 and 39 hours in oven reaching 334 and 388C, respectively. Latter can did not split open.
VI-1	1-double chopped chips.	Sprinkled seven days. After eight days in warm room at ~ 58C, placed in oven at ~ 95C.	Billet burned after 30 hours in oven reaching 483C. Can only slightly cracked.
VI-2	1-single chopped chips.	Sprinkled seven days. After eight days in warm room at ~58C, placed in oven at ~95C.	Billet burned after 42 hours in oven reaching 244C.
VI-3	1-double chopped chips.	Sprinkled seven days. After eight days in warm room at ~ 58C, removed can lid. After 40 days in warm room placed billet in oven at ~ 85C for ten days. Then raised oven temperature to ~93C for 32 days.	Billet did not burn. Can not split. Billet not cracked.
VI-4	4-double chopped chips and 5 single chopped chips.	After eight days in warm room at ~ 58C, removed can lids for remainder of 82 days in warm room.	No billets burned. Cans not split.
VII-1	2-fines and chips production billets cast in April or May, 1979.	On eighth day in warm room at ~ 58C removed can lids. On 22nd day in warm room, placed in oven at ~ 85C.	One billet burned after 52 hours in oven reaching 244C. The other billet burned after 120 hours in oven reaching 360C.
VII-2	1-fines and chips production billet cast in April or May, 1979.	On eighth day in warm room at ~ 58C removed can lids. on 40th day in warm room, placed in oven at ~ 85C for ten days. Then raised oven temperature to ~ 93C.	Billet burned after 93 hours in ~ 93C oven reaching 222C.

Table I

B-12

UNI-1454

<u>Test No.</u>	<u>Number and Type of Billets</u>	<u>Treatment</u>	<u>Results</u>
VII-3	3-fines and chips production billets cast in April or May, 1979.	On eighth day in warm room at ~ 58C removed can lids. Remained in warm room for 82 days.	No billets burned. Cans not split.
VIII-1	2-fines and chips production billets cast In April or May, 1979.	Billets from Test VII-3 that were placed in oven for 105 hours at 84-93C and 187 hours at 80-89C.	No billets burned. Cans not split.
VIII-2	2-fines and chips production billets cast in April or May, 1979.	Lids removed. After eight days in warm room at up to 58C, placed in oven at 82-88C.	One billet burned after 162 hours in oven. Other billet did not burn after 19 days and can not split.

FIGURE B-1.

HEAT OF HYDRATION CURVES FOR THREE TYPES OF CONCRETED BILLETS IN WARM 303-K BUILDING

FIGURE B-2.

HEAT OF HYDRATION CURVES FOR THREE TYPES OF CONCRETED BILLETS DURING COLD WATER SPRINKLING IN 304 BUILDING

Figure B-3.

Appearance of First Test Billet to Autoignite. This Heavy Uranium Fines to Chips Ratio Billet was Not Cooled Prior to Being Placed in a Warm Room at 35-39 C. Note How Can Split at Folded Seam.

FIGURE B-4.

**AUTOIGNITION TEMPERATURE CURVE FOR A HEAVY
URANIUM FINES TO CHIP RATIO CONCRETED BILLET
CONTAINING TWO POUNDS OF UNMIXED FINES IN
CENTER OF BILLET, WATER SPRINKLED FOR
3 DAYS PRIOR TO OVEN TEST**

Figure B-5.

Appearance of Badly Cracked Test Billet that did Not Autoignite. This Heavy Uranium Fines to Chips Ratio Billet with Unmixed Fines had been Sprinkled for 3 Days Prior to Being Placed in a Warm Room at About 63 C.

Note Unmixed Fines at Bottom of Can.

FIGURE B-6.

TEMPERATURE EXCURSION OF URANIUM-CONCRETE BILLETS

Figure B-7.

Test Billet That Did Not Autoignite After 32 Days At 93 C. This chips only billet had been 1) sprinkled for 7 days, 2) placed in a warm room at about 58 C for 40 days and with the lid removed after 8 days, and 3) placed in an oven at about 85 C for 10 days. Then the temperature was increased to about 93 C for 32 days.

Note that the concrete billet surface was not cracked.

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