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THE EBR-II SKULL RECLAMATION PROCESS Part III. Skull-oxidation Equipment

by

W. E. Miller, G. J. Bernstein,
R. M. Fryer, R. F. Malecha,
M. A. Slawewski, and R. C. Paul

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Printed in the United States of America

Available from

Clearinghouse for Federal Scientific and Technical Information

National Bureau of Standards, U. S. Department of Commerce

Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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Chemical Engineering Division

October 1967

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ABSTRACT

The fuel discharged from the Second Experimental Breeder Reactor (EBR-II) is an enriched uranium-fissium alloy which is processed by melt-refining. The melt-refining process consists of melting the metallic fuel in a zirconia crucible and liquating the material for about 2 hr at 1400°C to remove most of the fission products by volatilization and oxidative slagging. Five to ten percent of the fuel processed in each melt-refining run collects as a residual skull in the zirconia crucible. Pilot-plant work on 20- to 30-g skulls showed that oxidation of the skull with an oxygen-argon mixture at a controlled temperature (700-800°C) was a satisfactory procedure for converting the skull to a powder. By this means, a relatively massive skull that adheres to the crucible can be converted to a free-flowing powder that can be poured out with a recovery of about 98%. Plant equipment for oxidizing 400- to 1000-g skulls was developed, installed in the EBR-II Fuel Cycle Facility, and has been used to process about 300 kg of skull material since its startup. The equipment consists of an electrically heated resistance furnace, an off-gas system, and process controls. The major design problem was to develop a small furnace that would burn the skull with minimum damage to the zirconia crucible. The size requirement was met through the use of an immersion-type heater, which projects into the crucible. Minimum crucible damage was achieved by using a control system that caused the skull to burn at a uniform rate. The activity levels of the volatile fission products from the skull-oxidation furnace have been sufficiently low to permit release of the gaseous effluent to the atmosphere through the 200-ft site stack.

I. INTRODUCTION

The nuclear fuel of the Second Experimental Breeder Reactor (EBR-II) consists of 52% enriched uranium alloyed with 5% fissium.*¹ When approximately 1.2% of the uranium atoms in the fuel have fissioned, it is discharged from the reactor and processed to remove fission products and to

*Fissium is a term that has been coined to represent a mixture of fission-product elements (atomic numbers 40 to 46), which, when alloyed with uranium, impart to the alloy desirable metallurgical and radiation-stability properties. In this fuel, concentrations of fission-product alloying elements are: 2.5 w/o molybdenum, 2 w/o ruthenium, 0.26 w/o rhodium, 0.19 w/o palladium, 0.1 w/o zirconium, and 0.01 w/o niobium.

restore its original metallurgical and nuclear properties. Processing is accomplished in the adjoining Fuel Cycle Facility,² which is an integral part of the EBR-II complex.

Fuel is processed by melt refining,^{3,4} which is one of several steps in the fuel cycle. In this step, the fuel alloy is melted and liquated for about 2 hr at 1400°C in a lime-stabilized zirconia crucible. The fuel alloy is then poured into a graphite mold to produce an ingot which is used for the production of new fuel pins. Melt refining removes three classes of fission products from the fuel.¹ The inert fission gases xenon and krypton are released on melting.² Fission products, such as bromine, iodine, cesium, and rubidium, which have high vapor pressures at 1400°C, are volatilized.³ The rare-earth metals, such as samarium and neodymium, which form oxides more stable than uranium dioxide, are oxidized by the oxygen in the zirconia crucible. These rare-earth oxides remain with the crucible when the alloy is poured into the mold.

The skull that remains in the melt-refining crucible is made up of an oxide dross and unpoured metal, including about 7% of the uranium originally charged to the melt-refining process. Since approximately 2.5 kg of skull material is generated each week in the Fuel Cycle Facility,⁵ the value of the enriched uranium necessitates recovery of the skulls from the waste crucibles.

The process chosen for the recovery of skull material from spent melt-refining crucibles must satisfy four objectives:

- (1) In the melt-refining process, the normal yield is about 93%. To achieve the desired 99.7% overall yield for a 10-kg melt-refining charge, 94% of the uranium must be recovered from skulls weighing 500 g.
- (2) The removal process should not introduce gross contaminants into the recovered material. Although some contamination of the product by zirconia from the crucible is inevitable, the extent of this contamination should be held within an acceptable limit.
- (3) The form of the product should be suitable for subsequent recovery processes. An oxide powder is an acceptable feed for either pyrochemical or aqueous recovery processes.
- (4) The process must be suitable for remote operation.

The method chosen for skull removal was complete oxidation of the skull.⁶ Complete oxidation produced a divided solid, which poured easily from the zirconia crucible. When properly controlled, the oxidation process caused minimum additional damage to the zirconia crucible and thus avoided introduction of excess zirconia fragments into the skull oxide.

Several other skull-removal processes were examined.⁶ Physical removal of the skulls from crucibles was not practical. In this method, the crucible was broken into fragments to free the skull. This procedure invariably introduced gross amounts of zirconia into the skull, and this zirconia could not be removed by any method that was suitable for remote operation. Nitridation⁷ of skulls was successful, but nitridation was considerably slower than oxidation. Repetitive cyclic treatments with oxygen and hydrogen were also successful, but this procedure was more complicated than treatment with oxygen alone. Partial oxidation to free the skull from the crucible was moderately successful, but the extent of oxidation required in any particular case was not predictable. A minimum of about 25% of the skull material had to be oxidized to release the skull from the crucible. Partial oxidation was most successful when the crucible was inverted. However, this procedure introduced serious problems with remote-equipment design, and since a considerable degree of oxidation was required anyway, partial oxidation was supplanted by complete oxidation.

This report deals with the design and operation of skull-oxidation equipment and the important factors that influenced the design. The equipment described has been in operation in the Fuel Cycle Facility for three years and has been used to process about 300 kg of skull material.

II. DESCRIPTION OF CRUCIBLE AND SKULL

A. Crucible

The crucibles used in melt refining are $\sim 9\frac{1}{2}$ in. high and have a $5\frac{1}{8}$ -in. ID, $6\frac{3}{8}$ -in. OD, and $8\frac{1}{2}$ -in. inside depth. The crucibles are obtained commercially and are made of pressed and sintered, high-density, stabilized zirconia grain. The composition of the grain is ZrO_2 -5% CaO and less than 3.7% total Fe_2O_3 , HfO_2 , SiO_2 , TiO_2 , and Al_2O_3 . The melt-refining process depletes the oxygen in the zirconia crucible wall adjacent to the melt and lowers the strength of the wall. This loss of structural strength in the crucible wall results in two types of failures. In the first type, the crucible cracks quite severely; in the second, its inner surface in the area of the skull abrades much more readily than that of an unused crucible. Because of the cracking, the used melt-refining crucible is placed in a close-fitting stainless steel container which prevents an undue amount of further degradation from thermal shock and handling in the skull-oxidation step.

B. Skull

A skull is made up of two distinct parts (as shown in Fig. 1). One part consists of the skin, which remains on the crucible wall and contains some oxide and some metal. The height of a skull is governed by the charge size. For a 10-kg melt-refining charge, the skull height is about $1\frac{3}{4}$ in.

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Fig. 1. Skull Remaining in Crucible
after Melt Refining

When the metal alloy is poured from the crucible, a tongue that is left on one side of the crucible becomes part of the skull. A dross layer or skin may also be formed on top of the molten metal during melting. Usually this layer remains intact, although it may be displaced from its original position by the pouring process.

The other part of the skull is an unpoured button of metal. This metal is prevented from leaving the crucible as a liquid by a dam formed by the oxide dross. When the crucible is returned to the vertical position after pouring, this metal collects in the bottom of the crucible and coalesces into a button. The button is roughly in the form of a disk

1 to 3 in. in diameter and $1/4$ to $1/2$ in. thick. The button is usually bonded to the skull, which lines the inner surface of the crucible. The weight ratio of button material to skin material varies from run to run, but is usually about 10:1.

Table I gives the composition of a typical skull as estimated by Johnson *et al.*⁶ The estimated self-heating rate from the decay of

TABLE I. Composition of Typical Crucible Skull
Charged to Oxidation Furnace

Basis: ~700-g Crucible Skull

Constituent	Weight, g	Constituent	Weight, g
U	521.0	Ru	11.3
UO ₂	65.9	Rh	1.8
Pu	6.4	Pd	1.2
PuO ₂	0.8	Ag	<0.1
Rb ₂ O	<0.1	In	<0.1
SnO	5.4	Sn	<0.1
Y ₂ O ₃	3.0	Sb	<0.1
Zr	9.4	Te	1.4
ZrO ₂	1.4	Cs ₂ O	0.6
Nb	0.6	BaO	6.4
Mo	14.6	(RE) ₂ O ₃ ^a	46.6
Te	2.2	I ^b	-

^aRE designates the rare-earth fission-product group.

^bAbout 350 Ci of iodine are present.

radioactive fission products in the skull is 320 W. This assumes that the fuel has been irradiated to 1.2 a/o burnup and cooled 15 days. It also assumes that all the beta activity and 40% of the gamma activity are absorbed.

Figure 2 shows the cup-like structure of part of a typical skull. This skull was removed from the crucible by partial oxidation. The missing portions of the cup were oxidized to form the oxide powder shown in the figure. Also shown in this figure is a portion of the slag layer that covered the top of the melt during melt refining. This layer was also partially oxidized. A small button of unpoured metal appears at the bottom of the skull. This figure shows the nonuniform nature of the product of the oxidation process.

108-5998

Fig. 2. Partially Oxidized Skull Removed from Crucible

III. OXIDATION METHODS AND PROCESS CONTROL

Information collected in pilot-plant work⁶ was of great value in determining the design of the skull-oxidation furnace and the furnace-control system. The burning-rate data collected in the small-scale, pilot-plant studies did not apply directly to full-size skulls. However, the pilot-plant work did establish the fact that the size of the skull has a considerable effect on burning rate. Pertinent burning characteristics that had been determined in the pilot-plant work affected the plant-scale equipment design and are itemized below.

1. In the pilot plant, burning of the skulls in oxygen diluted with argon was much more satisfactory than burning of the skulls in oxygen alone. When skulls were burned in undiluted oxygen, large initial temperature excursions occurred, burning was erratic, and excessive crucible fragmentation, as well as sintering of the oxide product, resulted.

2. The instantaneous oxidation rate for a particular skull, burned in oxygen diluted with argon, was a function of the oxygen concentration and of the percent conversion of the metal to oxide.

3. Oxidation rate was not influenced greatly by temperature variations between 700 and 850°C. For sustained temperatures above and below this range, the rate of oxidation generally decreased.

4. Rates of oxidation varied somewhat from skull to skull. This effect prevented the development of a rigorous correlation of rate data. However, general trends were recognizable and reproducible.

The skulls, which are self-heating because of fission-product decay, become partially nitrified when they are exposed to the argon-5% nitrogen atmosphere in the Fuel Cycle Facility processing cell. Skulls that had been partially nitrified were easily converted to oxides by burning in oxygen. This procedure resulted in the liberation of nitrogen, and required that the equipment be designed so that the cover gas in the furnace be changed continuously.

To analyze the effect of oxidation of a nitrified skull in a closed system (gas flow in, but no gas flow out), we must consider a specific case. Consider the oxidation of a 700-g skull, which is 30% converted to nitride. About 0.7 g-mole of nitrogen would be liberated when the nitride is converted to oxide. The oxidation furnace contains about 0.35 g-mole of oxygen-argon mixture at the operating temperature and a 1 atm pressure. On conversion of the nitride to oxide, the nitrogen liberated would, by itself, produce a pressure of 2 atm in the furnace. The effect of oxidizing a nitrified skull in a closed system is to decrease the percentage of oxygen, since the concentration of nitrogen increases as the oxidation proceeds. What is really desired (as will be discussed later) is an increase in the percent of oxygen as oxidation proceeds. This can be accomplished with a flow-through system, but not with a closed system.

The curve in Fig. 3, which is based upon data from the pilot plant, shows the effect of the extent of oxidation on the burning rate of an unnitrified skull. The skull was burned at constant pressure in an atmosphere with a constant mole fraction oxygen. The slope of the curve at any point is a measure of the instantaneous rate of conversion of metal to oxide. The rate decreased markedly with the extent of conversion. Table II was prepared from the data in Fig. 3. The data show that an atmosphere of constant oxygen composition would result in an excessively long burning time.

Fig. 3

Oxidation of 20-g Skull at 700°C
in Gas of Fixed Composition.
Mole fraction oxygen: 0.33.
Total pressure: 600 mm.

TABLE II. Burning Rates Calculated from Fig. 3

Time Period	Average Oxygen Consumption Rate, g/min	Average Uranium Conversion (U-U ₃ O ₈) Rate, g/min
First minute	0.45	2.5
First 5 min	0.29	1.6
First 10 min	0.18	1.0
First 30 min	0.07	0.4

Figure 4, which is based upon pilot-plant data, illustrates how oxygen concentration affects the burning rate at conversion values of 10 and 20%. The three curves are for three separate skulls. Each skull was burned in an oxygen-argon atmosphere in which the mole fraction oxygen and the total pressure were held constant. The slopes of these curves (which represent the conversion rate) are noted on the curves at two conversion levels. At 10% conversion, the rates of conversion are 1.65, 0.41, and 0.13%/min for oxygen-argon gas mixtures of 0.25, 0.07, and 0.05 mole fraction oxygen, respectively. These curves show that the rate of burning at different conversion levels can be controlled by proper manipulation of the oxygen concentration in the oxygen-argon mixture. Finding a reliable way to do this was a major problem in the design of the furnace control system.

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Fig. 4. Oxidation of Three 25-g Skulls at 750°C in Gases of Fixed Composition

IV. DESIGN OF FURNACE-CONTROL SYSTEM

A. Introduction

In the design of a control system for the skull-oxidation furnace, the heat balances around the furnace were analyzed. Approximately 1 kW of heat is required to maintain a typical skull (400 to 1000 g) at the desired 700°C temperature. This heat is supplied by three sources: (1) fission-product decay heat within the skull and crucible, (2) heat produced by the exothermic oxidation reaction, and (3) supplemental electrical heating. The fission-product decay heat rate is estimated to be 0.32 kW for a typical skull, assuming absorption of 40% of the gamma activity and 100% of the beta activity. The conversion of metallic uranium to U_3O_8 at ~700°C liberates 850.3 kcal per mole of U_3O_8 .⁸ To oxidize a skull containing 700 g of metallic uranium in the desired period of 8 to 10 hr, the average oxidation rate corresponds to the conversion of about 1.5 g of uranium metal per minute. This oxidation rate results in a heating rate of approximately 0.12 kW. Therefore about 0.56 kW of supplemental electrical heat is required for a uniform burning rate. However, because of the heterogeneous nature of a skull, high burning rates are likely to occur sporadically, causing fragmentation of the crucible by thermal shock. Since the furnace is cooled only by natural convection of the atmosphere on its outside surface, the temperature of the furnace cannot be controlled if the instantaneous burning rate exceeds the average rate by a factor of 5.7 for a significant period of time.* Because of these considerations, the system was designed for a constant burning rate.

B. "Ideal" System

An "ideal" system (i.e., a system in which the gas composition varies with time) was considered. Design of such a system would have required data to predict precisely how the composition should be varied to achieve a constant burning rate. This type of control system was not used for the following reasons:

(1) Pilot-scale work had shown that burning characteristics varied with skull weight. In the plant, skull weights can vary by as much as a factor of two, and a great deal of plant-scale data would be required to make predictions.

(2) The effect of radiation on skull burning rates was unknown.

(3) Pilot-scale work had shown that burning characteristics varied somewhat among skulls of the same weight.

*With 0.32 kW of fission-product decay heat and $0.12 \times 5.7 = 0.68$ kW from the heat of reaction, the furnace reaches its maximum heat-dissipation capability of 1 kW at 700°C.

Accordingly, a control system based on changing the oxygen concentration as a function of time was rejected as impractical. Instead, the control system was designed to operate on an "oxygen-demand" basis.

C. Demand System

To understand how a demand system works, consider an oxidation furnace of constant volume and constant temperature distribution, within which a skull is being burned. At a particular time, there is a given mixture of oxygen and argon in the furnace, and the skull is at some degree of conversion from metal to oxide. If pure oxygen is fed to the furnace at a constant rate, the pressure in the furnace rises, remains constant, or falls, depending on whether oxygen consumption by the skull is less than, equal to, or greater than the oxygen feed rate. An increase in furnace pressure can be used as a signal to bring about an oxygen enrichment in the furnace atmosphere. In essence, the objective of this type control is to cause the skull to consume oxygen at a rate equivalent to the oxygen feed rate. If, at any time, the skull burning rate is too low, the control system produces an oxygen enrichment. This may be called a "demand" system since the control system demands that the skull burn at a constant rate; and in turn, if the skull does not respond, a demand is made for further gas enrichment. Provision can also be made to decrease the concentration of oxygen if the actual burning rate exceeds the desired burning rate.

The "demand" system accomplishes the same objective as the "ideal" system; that is, the oxygen concentration in the oxygen-argon mixture is raised as required to keep the skull burning at a constant rate. The "demand" system, however, has many advantages over the "ideal" system. The "demand" system requires no reference data to program the rate of oxygen addition since it adjusts the oxygen concentration automatically as required, rather than on a predetermined time basis as in the "ideal" system. The "demand" system will burn all skulls properly, regardless of differences in radiation effects, skull size, or burning characteristics. The remainder of this report deals with the design and operation of the "demand" control system and the skull-oxidation furnace.

V. DESCRIPTION AND OPERATION OF CONTROL SYSTEM

A. Description

Before describing the details of the control system, we will explain the furnace environment. The atmosphere in the Argon Cell of the Fuel Cycle Facility consists of argon containing up to 5% nitrogen. Water vapor and gases such as oxygen are present in concentrations of 40 ppm or less.⁹ The skull-oxidation furnace is opened within the Argon Cell to load the skull and crucible. When the furnace is subsequently closed and sealed, the atmosphere within the furnace is the same as the cell atmosphere. The oxidation process is then initiated by injecting pure oxygen into the furnace atmosphere.

Because oxygen is an undesirable contaminant in the Argon Cell atmosphere, effluent gases from the oxidation furnace cannot be discharged to the cell. Instead, they are collected in a holdup tank for subsequent disposal through the plant-exhaust gas system. The skull (before oxidation) contains some of the volatile and gaseous fission products such as ^{131}I , ^{137}Cs , and ^{133}Xe . A special in-cell filter removes ^{131}I from the effluent gas.

The filter consists of a vacuum-tight cylinder containing a high-temperature, high-efficiency AEC filter, followed by a 2-in. layer of activated charcoal.

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Fig. 5. Control-system Piping, Schematic Diagram

holdup-tank pressure. The outputs of the transmitters are displayed on the control panel in the operating corridor of the Argon Cell. The outputs of the transmitters also operate pressure switches,** which activate the solenoid valve operators for the control valves† in the process lines.

The explanation of the "demand" system given at the end of Section IV included nothing about how oxygen enrichment would be controlled. This could be done with proportional control to give instantaneous response. However, this type of equipment was not considered suitable for the specific application. The gas-discharge line from the furnace is expected to become highly contaminated with volatile fission-product residues, and valves in this line would be subjected to the same contaminating atmosphere. Proportional control valves would require more maintenance than simple on-off valves would. Therefore, to minimize maintenance on the active piping, cyclic on-off control was used, rather than proportional control.

*Taylor, Differential Pressure Transmitter, Models 339RF1, 339RF2.

**Minneapolis Honeywell, Pressuretrols.

†Associated Valve Company, Series 1193.

B. Operation

The operation of the control and off-gas system can best be described by referring to Figs. 5 and 6. Figure 6 shows the important events that take place during pressure cycles. Four furnace pressure levels are important

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Fig. 6. Graphical Representation of Events during Pressure Cycling

in the functioning of the control system. These are designated as P_1 , P_2 , P_3 , and P_4 in Fig. 6. The response of the system may be followed by noting the sequential points on Fig. 6 and the lines connecting these points. When the pressure level in the furnace decreases to P_2 (as at point 1), the furnace is rapidly evacuated by the vacuum system to pressure level P_3 (as at point 2). This change causes the oxygen feed to start. Between points 2 and 3, oxygen is being fed at a constant rate. The pressure in the furnace rises, remains constant, or falls, depending on whether the oxygen consumption rate resulting from burning of the skull is less than, equal to, or greater than the oxygen feed rate. The time required for the pressure to rise from point 2 to point 3 depends entirely on the rate at which the skull consumes the oxygen. Between points 2 and 3, the oxygen consumption rate is less than the oxygen feed rate, and the pressure rises.

When the pressure level rises to P_1 (as at point 3), the oxygen feed is cut off. The consumption of oxygen by the burning skull causes the pressure level to decrease to P_2 (at point 4), at which time the furnace is rapidly evacuated again to pressure level P_3 (as at point 5). The basic cycle traced between points 1 and 5 is repeated as long as the skull continues to burn. The furnace atmosphere is incrementally enriched by removing a portion of the oxygen-argon mixture from the furnace (evacuation from pressure level P_2 to P_3) and replacing the mixture with pure oxygen.

If, during one of the pressure cycles, the skull consumes oxygen more rapidly than it is being fed, the pressure may decrease to pressure level P_4 (as at point 6). This action shuts off the oxygen feed and opens an argon feed to quench the burning. When the pressure level increases to P_3 the argon quench is terminated and the oxygen feed is restored. The argon quench is seldom required, but is provided as a safety feature to ensure that rapid combustion, if it starts, does not continue.

In later pressure cycles, such as between points 7 and 8, the pressure rises more rapidly than in earlier burning. This condition results from the fact that the rate of burning of the skull has decreased despite the increased oxygen concentration. (The rate of reaction is reduced because the oxygen must diffuse through the accumulating layer of oxide.) Also, in the later cycle, the pressure drops more slowly from P_1 to P_2 . This effect

can be seen by comparing the slope of the curve between points 8 and 9 with the slope of the curve between points 3 and 4. Since there is no oxygen feed between P_1 and P_2 , the slow change in pressure results only from the reduced rate of oxygen consumption by the burning skull. Still later in the burning period; when oxidation is essentially complete, the rate of pressure rise between P_3 and P_1 , as noted between points 10 and 11, is a function of the oxygen feed rate only. After point 11, there is essentially no pressure decrease, which indicates that the burning reaction has been completed.

The preceding discussion shows that the pressure is allowed to drop (because of oxygen consumption by the burning skull) from P_1 to P_2 in each cycle (before partial evacuation). This procedure provides automatic cutoff of the oxygen feed at the end of a run. This is an important feature because it allows the equipment to operate unattended and uses a minimum amount of oxygen. The quantity of oxygen used in the furnace should be kept to a minimum since the effluent gases from the furnace are collected in a holdup tank of limited size.

Selection of the pressure levels for operation of the control system was somewhat arbitrary. The narrower the span between P_2 and P_3 , the more closely the instantaneous burning rates are controlled. However, a narrower span results in increased valve cycling and, hence, accelerated valve wear. The control pressure levels used in plant equipment are, therefore, a compromise. To minimize the risk of oxygen leakage from the oxidation furnace to the cell, the atmosphere of the skull-oxidation furnace is maintained at a negative pressure with respect to the cell atmosphere. The cell atmosphere itself is maintained at a negative pressure with respect to external atmospheric pressure.⁹ Therefore, the absolute pressure levels in the skull-oxidation furnace vary with atmospheric pressure. The pressure differentials between P_1 , P_2 , and P_3 are constant. In the EBR-II plant equipment, these values are: $P_1 - P_2 = 7.5$ mm Hg; $P_1 - P_3 = 65.0$ mm Hg.

C. Use of Information from Control System

A great deal of useful information can be obtained from pressure-time curves in the instrumentation record of a run. In the discussion below, Fig. 6, which shows the shape of such curves, is used as reference. For skulls that are not nitrided or in which the degree of nitridation is low, quantitative information may be obtained from the pressure-time curves as a run is in progress. Evolution of nitrogen from heavily nitrided skulls would change the shape of the curves and, consequently, interfere with an analysis of the curves. The following calculations can be made from the information provided by the curves:

1. Calculation of Instantaneous Burning Rate

For any point on the curve between points 2 and 3, let:

n = moles of oxygen present in the oxidation furnace, including the process lines isolated by the control valves (The line volume is small compared to the furnace volume);

K = oxygen feed rate, a known constant, moles/time;

B = oxygen consumption rate, moles/time;

t = time;

V = gas volume of the furnace, including the volume in the lines to the control valves;

T = average gas temperature in the furnace (Although temperature gradients exist in the furnace environment, specific locations remain at constant temperature during a run, and consequently the gas acts as though it were under isothermal conditions.);

R = gas constant.

The rate of change of the oxygen content of the furnace is then given by

$$\frac{dn}{dt} = K - B.$$

Since V and T are constants,

$$\frac{dn}{dt} = \frac{dp}{dt} \left(\frac{V}{RT} \right)$$

and

$$K - B = \frac{dp}{dt} \left(\frac{V}{RT} \right)$$

where dp/dt is the slope of the pressure-time curve. The oxygen consumption rate, B , can thus be determined since it is the only unknown. From this relationship, the conversion rate of uranium to uranium oxide (U_3O_8) is obtained directly.

2. Calculation of Oxygen Concentration

The atmosphere in the burning chamber is initially that of the cell (argon-5% nitrogen), and the only way this gas is removed from the furnace is by evacuation that takes place in the part of the cycle between points 1 and 2 or points 4 and 5 (see Fig. 6). In this part of the cycle, the pressure is reduced from P_2 to P_3 . The pressure is restored to P_1 by addition of pure oxygen. However, for these calculations the pressure at P_2 is the significant value. The partial volume of inert gas remaining in

the furnace after one evacuation is $(P_3/P_2) V$. After N evacuations, the partial volume of inert gas is

$$\left(\frac{P_3}{P_2}\right)^N V.$$

Therefore the volume fraction of inert gas is

$$\frac{\left(\frac{P_3}{P_2}\right)^N V}{V} = \left(\frac{P_3}{P_2}\right)^N.$$

The volume fraction of oxygen at any point on the pressure-time curve where the pressure is P_2 is given by

$$1 - \left(\frac{P_3}{P_2}\right)^N.$$

The concentration of oxygen at points such as 1, 4, and 9 (Fig. 6) can therefore be determined.

3. Calculation of Amount of Oxygen Pumped Out of Furnace

Let C_i = concentration of oxygen just before the furnace is partially evacuated. Then the amount of oxygen removed in any evacuation is given by

$$C_i V \frac{P_2 - P_3}{P_2}.$$

Since this is true for each evacuation ($C_1, C_2, C_3, \dots, C_N$), the total amount of oxygen removed from the furnace for all the evacuations is

$$C_1 V \frac{P_2 - P_3}{P_2} + C_2 V \frac{P_2 - P_3}{P_2} + \dots + C_N V \frac{P_2 - P_3}{P_2}.$$

Since $C_1 = 0$ at the start of a run, the total amount of oxygen removed from the furnace during a run is

$$V \frac{P_2 - P_3}{P_2} \sum_{i=2}^N C_i,$$

where the C_i 's are the calculated values of C from Subsection 2 above.

4. Calculation of Amount of Oxygen Consumed by Skull

Oxygen Consumed = Feed - Pump Out - Enrichment

Feed: The oxygen is fed at a constant rate when the oxygen-feed valve is open. A timer records the time interval during which the valve is open. The total oxygen fed is the product of feed rate and time.

Pump Out: The oxygen removed from the furnace during the evacuation cycles was obtained in Subsection 3 above.

Enrichment: A certain amount of oxygen remains in the furnace atmosphere at the end of the run.

The calculation methods outlined above were checked using the pressure-time curve recorded by the instrumentation during an actual run. Table III, which gives the oxygen material balance of the run, was prepared using the instrumentation record of the run. Although the balance could have been made at any convenient point along the time axis, the time chosen for the oxygen material balance was the entire run. If the entire run is used, the calculated value for oxygen consumed by the skull may be compared with the actual consumption as determined by the weight gain of the skull.

TABLE III. Calculated Oxygen Material Balance
for a 563-g Skull-oxidation Run

Oxygen fed	3.34 g-mole
Oxygen pumped out during evacuation cycles	3.07 g-mole
Oxygen enrichment	0.26 g-mole
Oxygen consumed by skull	2.71 g-mole

The oxygen consumption determined by the weight gain of the skull was equivalent to 2.84 g-mole. The calculation of oxygen consumption from Table III (2.71 g-mole) was in error by only about 5%. Oxygen utilization for this skull (fraction of total oxygen consumed by the skull) was 81%.

Figure 7 is a reproduction of data recorded on a strip chart from the plant instrumentation, with reference lines added. The uranium conversion rates equivalent to the slopes of these reference lines are noted. The slopes of these reference lines may be compared with the actual instrument trace as an indication of instantaneous uranium conversion rates that occurred during the controlled burning process. This comparison should be made only for those parts of the curve where the instrument trace is moving

from P_3 to P_1 . The reference lines were determined for the control condition that exists when the trace is moving from P_3 to P_1 ; therefore, they have meaning only in these regions. When the trace moves from P_1 to P_2 , the change in pressure results only from oxygen consumption while the oxygen feed valve is closed. When the trace moves from P_2 to P_3 , the pressure change results from evacuation of the furnace.

Fig. 7. Typical Pressure Record of Plant-oxidation Furnace

Figure 7 indicates that the first few cycles begin and end at pressures that differ from those in the remaining cycles. This difference arises from a manual override of the automatic control system. Manual override was necessary to initiate the burning condition. Oxygen was fed at a rate equivalent to a skull conversion rate of 1.69 g/min of uranium converted to U_3O_8 . During one period, the oxygen consumption equalled the feed rate. This resulted in a horizontal line on the trace. The maximum conversion rate was about 2.1 g/min. The last cycle clearly shows where the automatic oxygen shutoff feature came into play.

VI. OXIDATION-FURNACE DESIGN

A. Size Considerations

One important furnace-design consideration was size. Small size was desirable for several reasons. Because space within the Argon Cell and in the shielded area below the cell (subcell) is costly, the size of every piece of equipment within the cell must be minimized. The effluent gas from the furnace is retained in a holdup tank located in the subcell. The size of the tank depends on furnace size, since the volume of gaseous effluent from the furnace is proportional to the furnace volume. A specific limitation was placed on the diameter of the furnace bell jar so that it could be disposed of in a standard radioactive waste container if the furnace were to be damaged. The primary container for disposal of radioactive waste has an $11\frac{1}{4}$ in. ID; consequently, the bell-jar diameter was limited to 11 in.

As discussed previously, a supplemental heat source was required for the skull-oxidation furnace. The best way to supply heat to the furnace is with an immersion-type resistance heater placed inside the crucible containing the skull. Applying heat in this manner minimizes crucible damage because heat does not have to be driven through the refractory crucible wall to heat the skull. With the heater inside, the crucible wall serves as part of the furnace insulation. This also helps to limit the furnace size. The heater is rated at 1750 W at 230 V. It is spirally wound in a conical shape to provide the length of heater necessary and to take full advantage of the radiant heat from the coils. This heater shape provides the most efficient heating of the skull on both the wall and bottom of the crucible.

Furnace-seal design is important because the furnace must be opened and closed between runs. This is a remote operation, and the furnace must be tightly sealed when it is closed. Fusible-metal seals were used because experience has shown that these seals are practical for remotely operated equipment which must be tightly sealed.¹⁰ When fusible-metal seals are employed, the equipment must be designed so that process heat sources within a vessel do not melt the seal. Reducing equipment size makes the problem more acute, since the distance from the heat source to the seal is reduced.

The dimensions used in the furnace design were determined by calculation, and by a heat-transfer mockup test. The vertical temperature distribution along the outside of the shell of the mockup unit is shown in Fig. 8. The internal components of the furnace mockup are not shown in Fig. 8 since they are essentially the same as those in the furnace design discussed in detail below and shown in Fig. 9. Figure 8 indicates that the temperature at the bottom of the shell is 62°C. The melting point of the

fusible metal alloy* that contacts the bottom lip of the furnace is 138.5°C. Thus, a margin of safety of over 75°C is provided by making the overall length of the furnace 20 in. and locating the crucible and heater in the upper end, as shown in Fig. 9.

Fig. 8. Temperature Distribution on Outside Shell of Oxidation-furnace Mockup

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Fig. 9. EBR-II Skull-oxidation Furnace, Cutaway View

B. Mechanical Features and Remote Operation of Furnace

Figure 9 shows the important features of the furnace. The bell jar is 10 in. in diameter and 20 in. high. The furnace is built upon a rectangular steel base plate, 27 in. by 36 in. by 3/4 in. thick, which is mounted on short legs to elevate the furnace above the floor for process viewing. Locating pins fixed to the base plate allow the furnace assembly to be remotely installed in the Argon Cell using an electromechanical manipulator.¹¹ Gas inlet and outlet lines terminate in fusible-metal seals attached to the base plate.

The main body of the furnace consists of two major components: the container support and the bell jar. The crucible container fits inside the open-top container support, which is an insulated double-wall cylinder. A top view of the furnace with the bell jar removed is shown in Fig. 10. The bell jar is sealed to the container support by the fusible-metal seal. Experience has shown that stainless steel is poorly wetted by the fusible metal.¹⁰

*Bismuth 58%, tin 42%.

Consequently, a mild steel strip is welded to the bottom lip of the stainless steel bell jar, and a mild steel trough is welded to the stainless steel container support.

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Fig. 10. Oxidation Furnace with Bell Jar Removed

The bell jar is insulated at the top and has a sealed port through the top for the tubular resistance-heater lead. The resistance heater is suspended from the underside of the bell-jar top and extends down approximately 5 in. This position places the bottom turn of the heater coil well within the crucible when the furnace is assembled and ready for operation.

The crucible is remotely removed from the melt-refining furnace with a special set of manipulator-operated tongs. The crucible is subsequently placed in a close-fitting stainless steel container, which holds the crucible during the skull-oxidation process. The container is handled with tongs, which grip the container flange. The container is then placed in the container support of the skull-oxidation furnace. Equipment for these operations is shown in Fig. 11. After the fusible-metal seal is molten, the bell jar, which is hung on a stand at the rear of the furnace base plate, is

lifted by the manipulator over the container support and lowered into the molten metal seal. The molten seal is then allowed to solidify, and the oxidation process is carried out. After the skull has been oxidized, the atmosphere within the bell jar is purged with argon before the bell-jar

seal is remelted. The bell jar may then be removed from the seal and placed in the position shown in Fig. 11.

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Fig. 11. Remote Placement of Crucible and Stainless Steel Container into Oxidation Furnace

"tongues" are used to guide and position the plug for insertion in the receptacle, which has two slots, one wider than the other. Tapered guide pieces on the receptacles are sized so that the plug is fully aligned before electrical contact is made. Identical guide pieces are located on receptacles on the service-sleeve feed-throughs.

Both connectors shown in the upper parts of Figs. 12 and 13 serve a Chromel-Alumel thermocouple, which is attached to the upper right-hand connector. This thermocouple is used to measure and control furnace temperature.

The crucible and the oxidized skull (still in the stainless steel container) are removed from the furnace and placed in the oxide dumper. An inverted receptacle is then placed on top of the crucible, and the entire assembly is inverted, causing the oxide to fall into the receptacle.

Electrical connections to the top of the oxidation furnace are shown in Figs. 12 and 13. The connections are made from the furnace to the service feed-throughs by means of cable jumpers. The service end of the jumper is identical to the furnace end shown in Fig. 12. This method of connecting power and instrumentation leads is used throughout the Argon Cell for ease of remote handling.

Special holders for both thermocouple and electrical plugs are formed from sheet steel so that two "guide tongues," each of a different thickness, protrude from the sides of each plug. These

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Fig. 12. Power and Thermocouple Connectors in Place on Bell Jar

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Fig. 13. Top of Bell Jar with Power and Thermocouple Connectors Removed

The connector shown in the upper left in Figs. 12 and 13 is an extension jumper, which connects the instrumentation lead wire to the receptacle of the right-hand connector. The formed sheathed thermocouple is attached to the right-hand connector (see Fig. 13) so that the thermocouple can be replaced by removing the connector in the event of failure. The thermocouple is inserted into a well, the end of which is located within the coiled heater of the furnace. Both the plug and the receptacle are commercially available units.* Connection between the two thermocouple connectors is made with a short piece of extension cable visible below the two receptacles.

The connector shown in the foreground of Fig. 12 provides the heater-power connection between the furnace and the service feed-through. The leads are type AA** insulated cables covered with braided-asbestos sleeving. The plug and receptacle use ball-and-spring-loaded socket-type contacts rated at 70 Amps.† The contacts are placed in fabricated lava insulators, which are in turn placed in the special holders.

C. Control Panel

The furnace control panel, shown in Fig. 14, provides control for the sequence of operations necessary to accomplish a complete burning cycle in the oxidation furnace. For each operation the panel has a corresponding control position, which is selected by the switch at the top of the panel. The operations and functions of the panel are enumerated and briefly discussed below in terms of the six control positions and special features of the system.

1. FURNACE LOAD Operation

During the FURNACE LOAD operation, the oxidation furnace is opened after venting to the cell atmosphere and melting the freeze seal. The furnace is then loaded with a crucible containing a skull, after which the furnace is closed and the seal is frozen.

2. STARTUP Operation

In the STARTUP position, the vent is closed, and power is applied to the oxidation furnace to raise its temperature to the normal operating level. The furnace-discharge valve opens periodically to relieve the pressure of the expanding gases in the furnace during heat-up.

3. NORMAL RUN Operation

At the beginning of the NORMAL RUN operation, the oxidation furnace contains cell gas at furnace operating temperature. Oxygen feed

* Thermo Electric Company, Inc., Models P-MESS-CL and J-MESS-CL.

** Unimpregnated asbestos insulation rated for 200°C operation. See National Electrical Code, ASA C1-1965.

† Cole Electric Co., Model 101055.

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Fig. 14. Oxidation-furnace Control Panel

into the furnace is initiated. The control system periodically opens and closes the oxygen-feed valve and the furnace-discharge valve. The frequency of valve cycling varies, depending on the oxygen-feed rate, the oxidation rate, and the nitrogen-liberation rate. When oxidation is complete (no further oxygen consumption), the oxygen feed ceases.

4. SPECIAL RUN Operation

The SPECIAL RUN position provides for the possible necessity of oxidizing large pieces of scrap uranium, and affords added flexibility in burning normal skulls. For scrap burning, the scrap is not likely to be heavily nitrided, and gas will not be discharged from the oxidation furnace during the entire reaction period. After the burning operation is initiated in the NORMAL RUN position, the control is switched to the SPECIAL RUN position, and the control system maintains pressure in the furnace by adding oxygen as it is reacted. This procedure does not increase oxygen concentration as in the NORMAL RUN position.

5. ARGON PURGE Operation

During the NORMAL RUN cycle, cessation of oxygen feed indicates that the oxidation is complete. The oxidation furnace at this time contains gas rich in oxygen. The control system can then be placed on ARGON PURGE, which sweeps the oxygen from the oxidation furnace into the holdup tank. The argon purge is automatically terminated when the pressure in the holdup tank reaches a preset level due to gas accumulation.

6. HOLDUP TANK DISCHARGE Operation

The gases from one run in the oxidation furnace are accumulated in the 13-ft³ holdup tank. The holdup tank is emptied by pumping out and discharging the gases to the Fuel Cycle Facility 200-ft stack, where they are diluted with 60,000 cfm of stack gas. A key switch on the panel must be unlocked to accomplish the HOLDUP TANK DISCHARGE operation, which is performed only when atmospheric conditions are favorable for discharge.

D. Special Features

Since oxygen must not be permitted to leak into the inert atmosphere of the Argon Cell, a differential pressure switch is located across the oxygen flow-control needle valve to detect any valve leakage while the furnace is open or vented. If there is leakage, an alarm is given by a flashing light and a bell. The bell can be silenced, but the flashing light remains on until the leak is corrected.

To sense a rise in furnace pressure whenever the furnace is closed and no run is being made (including the OFF position), the furnace

differential-pressure transmitter actuates a pressure switch and gives an alarm whenever the pressure differential between the cell and the furnace (which is maintained at a negative pressure relative to the cell) becomes 3 mm Hg or less. Thus, leakage of either the argon or oxygen valves can be detected.

Two timers on the operating panel are reset to zero before each run. One timer indicates accumulated time of oxygen flow; the other indicates accumulated time of argon flow. This information is required to make the material balances and calculations discussed in Section V of this report. Figure 7 shows the type of information recorded.

A two-point Chromel-Alumel temperature indicator and controller is also provided (range 0-1000°C). The lower set point (approximately 700°C) prevents oxygen from being fed into the system until the furnace temperature reaches this point. The upper set point (750°C) controls the furnace-heater temperature. The unit can also be used to monitor the furnace-seal temperature by operating a switch located above the controller. In conjunction with the temperature indicator and controller, a saturable reactor is provided for adjusting heater power. Proper adjustment of the heater-power input decreases the on-off cycling of the temperature indicator and controller and provides uniform operation.

VII. OPERATING EXPERIENCE

Between July 1964 and March 31, 1967, 262 enriched skulls were processed through the skull-oxidation furnace in the Fuel Cycle Facility. The current production rate is 14 skulls per month, the overall recovery of skull material averaging 97%. Table IV presents average values for the material balances on processed skulls. The ratio of oxide weight to skull weight indicates the amount of oxygen consumed by the skull. The oxidized skulls exhibit a dark gray appearance and are usually well powdered. Occasionally, soft "clinkers" appear in the product oxide.

TABLE IV. Average Skull-oxide Material Balance, Irradiated Fuel

Source of Skull	Skull Weight, g	ZrO ₂ in Oxidized Skull, ^a g	Percent Recovery of Oxidized Skull	Final Ratio, Oxide Weight/Skull Weight	Remarks
Irradiated Fuel (MR) ^b	800	35	97.4	1.17	In use, ~15% of the crucibles failed completely
Scrap Consolidation (MC or MR-C) ^c	900	5	97.2	1.18	

^aWhen the oxide is dumped from the zirconia crucible, it is difficult to differentiate (by weighing) the oxide left in the crucible from the zirconia that separates into the skull oxide. Therefore, the absolute values of these numbers are uncertain.

^bMR: Fuel Melt-refining Run.

^cMC: Scrap-only Run.

MR-C: Combined Scrap and Fuel Melt-refining Run.

After 215 runs, the spiral Calrod heater failed and was replaced. Otherwise, the furnace components have performed perfectly.

Some crucibles (~15%) that have been used to melt-refine highly irradiated fuel show an increase in height after skull oxidation. This condition is associated with separation of the crucible bottom from the cylindrical wall during skull oxidation. This separation occasionally resulted in complete crucible failure during the subsequent dumping operation. The cause of this separation is not known, but the condition is attributed to greater localized self-heating in the highly irradiated fuel. This can result in more extensive cracking of the crucible during melt-refining.

Xenon is the only volatile fission product that reaches the off-gas system downstream of the in-cell filter in significant quantities. Activity

TABLE V. Isotopes Detected in Off-gas from a Typical Skull-oxidation Run

Isotope	Concentration, $\mu\text{Ci/liter}$
¹³³ Xe	200-400
¹⁰³ Ru, ¹⁰⁶ Ru	0.4
¹³¹ I	0.01

from ¹⁰³Ru, ¹⁰⁶Ru, and ¹³¹I has been detected in the off-gas, but at very low levels (see Table V). Analyses generally indicate less than 1 Ci of total activity in the off-gas from each skull-oxidation run. Since health-physics regulations allow the release

of up to 100 Ci directly to the atmosphere (excluding ^{131}I), the discharge of the effluent gases from skull oxidation has not been a problem.

ACKNOWLEDGMENTS

We are indebted to others who aided in the work described in this report. Suggestions and guidance were provided throughout by J. H. Schraidt and M. Levenson. D. C. Hampson did some of the earliest equipment work. The pilot-plant work carried out by T. R. Johnson, R. D. Pierce, L. Burris, Jr., and R. K. Steunenberg formed the basis for control design, and the results of their work have been used extensively in this report. Trouble-free operation of plant equipment is due in no small part to J. O. Ludlow, who supervised its installation. A. C. Chandler provided valuable technical assistance.

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