AEC
RESEARCH
and
DEVELOPMENT
REPORT

BNWL-354
41-

**ENGINEERING DEVELOPMENT
OF THE SALT CYCLE PROCESS**

G. JANSEN, JR.
L. K. MUDGE
P. W. SMITH

DECEMBER, 1966

BATTELLE-NORTHWEST

BATTELLE MEMORIAL INSTITUTE / PACIFIC NORTHWEST LABORATORY

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

PACIFIC NORTHWEST LABORATORY

RICHLAND, WASHINGTON

operated by

BATTELLE MEMORIAL INSTITUTE

for the

UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

PRINTED BY/ FOR THE U. S. ATOMIC ENERGY COMMISSION

UC-10, Chemical Separations
Processes for
Plutonium and Uranium

ENGINEERING DEVELOPMENT
OF THE SALT CYCLE PROCESS

By

G. Jansen, Jr.
L. K. Mudge
P. W. Smith*

Chemical Development Section
Chemistry Department

December, 1966

FIRST UNRESTRICTED
DISTRIBUTION MADE

MAR 3 '67

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

*P. W. Smith transferred from the Hanford Laboratories
to the Chemical Processing Department of the General
Electric Company and is now an employee of Isochem Inc.

ENGINEERING DEVELOPMENT
OF THE SALT CYCLE PROCESS

ABSTRACT

The pilot plant production of electrolytic uranium dioxide and the development of equipment to be used in remote processing of irradiated mixed $\text{PuO}_2\text{-UO}_2$ fuels are presented. The process steps are fuel decladding, oxidation of UO_2 to U_3O_8 , dissolution in molten salts with chlorine and hydrogen chloride gases, electrolytic deposition of oxides, product purification, crushing and sizing, and off-gas treatment.

TABLE OF CONTENTS

LIST OF FIGURES	viii
LIST OF TABLES	xi
INTRODUCTION	1
SUMMARY	5
DECLADDING	7
Vibrational Decladding	8
Oxidative Decladding	11
Gas-Phase Chlorination of Zircaloy	13
Decladding by Sparging Molten Salts	16
Metal Replacement Reaction	18
Effect of Decladding on Electrolytic UO_2 Deposition	18
Chlorination of Stainless Steel	21
OXIDATION	21
SALT SYSTEM PROPERTIES	26
Phase Diagrams	26
Densities of Molten Salts	29
Electrical Conductivity of UO_2	29
Decomposition Potentials of UO_2Cl_2 and Salt Solvents	33
SODIUM CHLORIDE-POTASSIUM CHLORIDE PILOT PLANT OPERATIONS	35
Dissolution and Drying	35
Electrolysis	37
Dual Vessel Experiments	37
Evaluation of Electrolytic UO_2 Product	39
EQUIPMENT FOR PILOT PLANT OPERATIONS	47
Electrolytic Cell	47
Instrumentation	50
Reference Electrode Control System	50
Dryness Test Apparatus	51
Crucible Breakage Alarm	51
LEAD CHLORIDE-POTASSIUM CHLORIDE PILOT PLANT OPERATIONS	52
Dissolution	52
Drying	53

Electrolysis	58
Product Evaluation	64
LITHIUM CHLORIDE-POTASSIUM CHLORIDE PILOT PLANT OPERATIONS	66
Dissolution and Drying in the 80 Liter Salt Bath	66
Electrolysis and Product Evaluation from 80 Liter Pilot Plant Runs	71
Effect of Impurities on Deposit Crystal Structure	75
Hot Cell Prototype Operations	78
Product Purification	88
ELECTRODE EVALUATION	91
Anodes	91
Metallic Cathodes	92
Graphite Cathodes	94
CONTAINER EVALUATION	97
Metallic Crucible Materials	97
Fused Silica Crucibles	97
Fused Silica Vessel Failures	100
Other Nonmetallic Materials	101
Frozen Wall Systems	101
Pyrolytic-Graphite-Coated Crucibles	103
CODEPOSITION AND PARTITION	103
Cerium Stand-In for Plutonium	105
Codeposition of Nickel-UO ₂ Cermet	108
PRECIPITATION	111
Freeze-Valve Technique	111
Thorium Stand-In for Plutonium	111
Cerium Stand-In for Plutonium	112
CRUSHING AND SIEVING	114
Wet Crushing and Sieving System	115
Iler Disc Pulverizer	117
Press Crushing with Notched Blades	123
Parallel Plate Crushing	127
Multipurpose Fines Production, Sieving, and Blending Equipment	131
Ball Milling	139

OFF-GAS TREATMENT	139
Caustic Scrubber for the Salt Cycle Demonstration	141
Hypochlorite Destruction	141
Chlorine Recovery by Liquefaction	142
ACKNOWLEDGMENTS	143
REFERENCES	144

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Page No.</u>
1	Close-Coupled Plutonium Recycle System	2
2	Salt Cycle Process Development	4
3	Vibratory Decladding Apparatus	10
4	Oxidative Decladding Test Results	12
5	Gas-Phase Chlorination of Oxidized Zircaloy-2	15
6	Remote Oxidizing Equipment	24
7	Phase Diagrams of Molten Salt Solvents	27
8	Phase Diagram for $\text{KCl-PbCl}_2\text{-UO}_2\text{Cl}_2$	28
9	Phase Diagram for $\text{KCl-LiCl-UO}_2\text{Cl}_2$	30
10	Density of $\text{PbCl}_2\text{-2.5 KCl}$ with Added UO_2Cl_2	31
11	Electrical Conductivity of Electrolytic UO_2 Deposited from Equimolar NaCl-KCl at 700°C	32
12	Decomposition Potentials in $\text{PbCl}_2\text{-KCl-UO}_2\text{Cl}_2$ System	34
13	Pilot Plant Equipment for Production of Electrolytic UO_2 in Equimolar NaCl-KCl	36
14	Electrolysis with Intermittent Recirculation	40
15	Electrolysis with Continuous Recirculation	41
16	UO_2 Deposit from NaCl-KCl Salt Bath	43
17	Effect of Agglomeration on Screen Analysis of Electrolytic UO_2	44
18	Crystal Characteristics of UO_2 Deposited from NaCl-KCl	45
19	Eighty Liter Pilot Plant Salt Bath for $\text{PbCl}_2\text{-KCl}$ System	48
20	Dissolution of U_3O_8 in $\text{PbCl}_2\text{-2.5 KCl}$	54
21	Wetness Tests in $\text{PbCl}_2\text{-2.5 KCl}$ with 30 wt% Uranium	57
22	UO_2 Deposits from $\text{PbCl}_2\text{-2.5 KCl}$ Salt System	60
23	Cross Section of UO_2 Deposit from $\text{PbCl}_2\text{-2.5 KCl}$ Salt Bath	61
24	Mace-Type Crystals from the $\text{PbCl}_2\text{-2.5 KCl}$ Salt Bath	62
25	Dissolution of U_3O_8 in Equimolar LiCl-KCl in the 80 Liter Salt Bath	70

<u>Figure No.</u>	<u>Title</u>	<u>Page No.</u>
26	UO ₂ Deposits on Hastelloy D Cathodes from 80 Liter LiCl-KCl Salt Baths	72
27	UO ₂ Deposits on Graphite Cathodes from 80 Liter LiCl-KCl Salt Baths	73
28	Reference Potential Variation in Constant Current Electrolysis	76
29	Hot Cell Prototype Equipment	79
30	Dissolution of U ₃ O ₈ in 2.5 LiCl-1 KCl	82
31	Dissolution of U ₃ O ₈ in 2.5 LiCl-1 KCl with a Gas Lift.	83
32	Voltage-Current Relationships in the Hot Cell Prototype Equipment	84
33	Crystal Characteristics of Hot Cell Prototype Electrolysis Product	86
34	Typical Deposit from the Hot Cell Prototype Electrolysis Product	87
35	Platinum Electrode Sheathed with Quartz, Run CT-4	92
36	Effect of Corrosion of Nickel Electrode on UO ₂ Deposit	93
37	Electrode Stripping Apparatus	94
38	Pyrolytic Graphite Coating on a Pile Graphite Cathode	95
39	Comparison of Stripping of UO ₂ from Pyrolytic-Graphite- Coated Electrode with Stripping of a Pile Graphite Electrode	96
40	Temperature Profiles in the Salt Bath Mockup for the Salt Cycle Demonstration	98
41	Induction-Heated System After Several Days Operation with a Broken Quartz Crucible	101
42	Cross Section of a Graphite Susceptor with a Frozen Wall After Several Days Operation	102
43	Pyrolytic Graphite Crucibles After Testing at 600 °C for 13 Days	104
44	Codeposit with 50% Oxygen - 50% Chlorine Sparge	107
45	Deposit from a High Temperature Partition	109
46	Codeposits with Intermittent Electrolyses	110
47	Wet Crushing and Sieving System	116

<u>Figure No.</u>	<u>Title</u>	<u>Page No.</u>
48	Iler Disc Pulverizer	117
49	Variation of Gap Between Discs - Product from Iler Disc Pulverizer	118
50	Effect of Speed on Crushing with Iler Disc Pulverizer - Coarse Setting	120
51	Effect of Speed on Single Pass Crushing of Electro- lytic UO_2 with Iler Disc Pulverizer	121
52	Effect of Moisture on Crushing and Screening Operations with Iler Disc Pulverizer	122
53	Integrated Crushing of Electrolytic UO_2 with Iler Disc Pulverizer to Produce Large Size Fraction	124
54	Press for Dicing and Parallel Plate Crushing Tests	125
55	Product from UO_2 Dicer Operation at 500 psi Terminal Pressure	126
56	Effect of Pressure on Dicing of Electrolytic UO_2	128
57	Production of Large and Intermediate Size Particles by Integrated Dicing Operations, Comparison of Size Distribution with Iler Disc Pulverizer Product	129
58	Single-Pass Crushing with Parallel Plates - Effect of Step Size and Size Reduction	130
59	Effect of Batch Size on Parallel Plate Crushing	132
60	Integrated Parallel Plate Crushing of Electrolytic UO_2 - Comparison of 0.222" Step with 0.156" Step in Production of -4 + 10 Mesh Particles	133
61	Effect of Pressure on Production of Intermediate Fraction UO_2 Particles	134
62	Preparation of UO_2 Feed for Vibratory Compaction by Parallel Plate Crushing	135
63	Ball Milling of Electrolytic UO_2	140

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
I	Gas Phase Decladding Studies	14
II	Decladding by Gas Sparge in Molten Salts	17
III	Decladding with Metal Replacement Reaction	19
IV	Effect of Decladding on Electrolytic UO ₂ Deposition	20
V	Decladding of Stainless Steel	22
VI	Oxidation of UO ₂ in Prototype Oxidation Equipment	25
VII	Pilot Plant Electrolyses	38
VIII	Chemical Analyses of Electrolytic UO ₂ Produced from the NaCl-KCl System	42
IX	Pilot Plant Electrolyses in the Lead Chloride- Potassium Chloride System, Twenty Liter Salt Bath.	55
X	Pilot Plant Electrolyses in the Lead Chloride- Potassium Chloride System, Eighty Liter Salt Bath.	63
XI	Effect of Hydrogen Treatment for 10 Hours at 1000 °C on Salt Content of Electrodeposited UO ₂	65
XII	Pilot Plant Electrolyses in the Lithium Chloride- Potassium Chloride System	67
XIII	Effect of Impurities on Electrolyses in Lithium Chloride-Potassium Chloride	77
XIV	Hot Cell Prototype Electrolyses	80
XV	Chemical Analysis of Composite Product from LiCl- KCl Pilot Plant Operations	89
XVI	Chloride Analyses in Aqueous Washing Studies	90
XVII	Corrosion of Metals in the Salt Cycle Environment.	99
XVIII	Cerium Stand-In for Plutonium in UO ₂ Depositions.	106
XIX	Fines Production by High-Speed Impaction	137
XX	Sieving Studies in Multipurpose Equipment	138

ENGINEERING DEVELOPMENT
OF THE SALT CYCLE PROCESS

INTRODUCTION

The Salt Cycle process was developed at Hanford as part of the Plutonium Recycle Program to reprocess $\text{UO}_2\text{-PuO}_2$ mixed oxide fuels for recycle to thermal reactors. In the recycle scheme short-cooled, irradiated fuel is reprocessed with a minimum number of remote manipulations. The central step in the process is the electrolytic deposition of crystalline, reactor-grade $\text{UO}_2\text{-PuO}_2$ solid solutions from molten chloride salts. The engineering development of the unit operations of the Salt Cycle process; such as decladding, dissolution, drying, off-gas treatment, electrolysis, and crushing, sizing and purification of the product; is described in detail here. Equipment for remote operation of the process was designed and tested, and several hundred pounds of electrolytic UO_2 that met reactor specifications were produced for evaluation as nuclear fuel.

One close-coupled plutonium recycle system that was considered for application of the Salt Cycle process is shown in Figure 1. The system is based on a zoned reactor which is fueled with unirradiated, slightly enriched UO_2 fuel elements and recycle $\text{UO}_2\text{-PuO}_2$ fuel elements containing lower enrichment uranium. A zoned reactor reduces fuel fabrication costs by minimizing the number of remotely fabricated recycle fuel elements. For this system the process should have the capability of (1) recovering the plutonium from the depleted recycle uranium in the irradiated $\text{UO}_2\text{-PuO}_2$ fuel elements, (2) combining on a molecular scale the recovered plutonium with the plutonium and a portion of the uranium from the irradiated UO_2 fuel elements, and (3) producing a $\text{UO}_2\text{-PuO}_2$ mixture which has physical properties suitable for re-fabrication and is relatively free of neutron poisoning fission products.

Because the Salt Cycle process has been specifically developed for reprocessing irradiated, short-cooled $\text{UO}_2\text{-PuO}_2$ mixed oxide nuclear fuels, an economic study of the relative merits of close-coupled, remote processing and central-plant processing has been made by R. W. McKee.⁽¹⁾ The first stage in the

FIGURE 1
Close-Coupled Plutonium Recycle System

development of the process was the production of electrolytic UO_2 from molten chloride salt baths. This step has applications in itself to the winning of high density UO_2 from uranium ores,⁽²⁾ and a preliminary economic evaluation of the costs of producing electrolytic UO_2 has been made by P. W. Smith.⁽³⁾ The preparation costs of solid-solution $\text{UO}_2\text{-PuO}_2$ by electrodeposition from molten chloride salt baths were evaluated by W. R. Bond,⁽⁴⁾ because solid-solution mixed oxides are desirable in fast reactors for control purposes. The preparation of an unique high density, crystalline PuO_2 by precipitation from molten salt baths containing uranium has been demonstrated in laboratory equipment.⁽⁵⁾

This is the second of a series of terminal development reports of the Salt Cycle process. The first part⁽⁶⁾ deals with plutonium chemistry and contains a bibliography of the uranium chemistry of the Salt Cycle process. This report deals with the engineering development of the unit operations necessary in the Salt Cycle process. The third report⁽⁷⁾ deals with the pilot plant demonstration of the process in a high-level radiochemical facility. The fourth report will detail remote refabrication of the fuel elements and the still unfinished in-reactor performance of the Salt Cycle product as a nuclear fuel.

This report is organized around the development of the unit operations shown in Figure 2. Because of contamination-control limitations in the pilot plant, plutonium was not used experimentally and stand-ins were employed where necessary. In the final version of the process, the $\text{UO}_2\text{-PuO}_2$ is removed from fuel rods by vibratory decladding, the UO_2 is oxidized to U_3O_8 , and the mixed oxide is dissolved in molten lithium chloride-potassium chloride by chlorine and hydrogen chloride gas. When uranium is to be separated from plutonium, the UO_2 may be electrodeposited alone in the presence of a hydrogen chloride gas sparge, or the PuO_2 may be precipitated alone by oxygen-chlorine or hydrogen gas sparges. Make-up UO_2 or PuO_2 may then be added to the bath, usually as an irradiated fuel element, and a $\text{UO}_2\text{-PuO}_2$ mixture electrodeposited with an oxygen-chlorine gas sparge. The mixed oxide is stripped from the electrode, crushed, washed with water, reduced with hydrogen if necessary, and sized for vibratory compaction into fuel elements.

EQUIPMENT AND MATERIALS DEVELOPMENT

FIGURE 2
Salt Cycle Process Development

SUMMARY

The engineering development of the unit operations used in the Salt Cycle process is detailed in this report. The development primarily involved pilot plant operations in the production of electrolytic UO_2 and the design and evaluation of equipment to be used in remote operations for recycle of irradiated mixed oxide fuels.

Vibratory decladding with an air hammer was selected as the primary technique for fuel-cladding separation because of its short time cycle, effectiveness in removing all of the fuel from the cladding, and minimal waste disposal problems. For cold-swaged UO_2 , decladding times as short as two minutes for a 0.5-in. diam by 4 ft-long rod were demonstrated in remotely operable apparatus with no appreciable formation of radioactive dust. Chlorine gas (diluted with nitrogen for temperature control) was selected as the backup chemical decladding technique for Zircaloy-2 decladding. Scouting studies with oxidative decladding, and decladding of Zircaloy-2 and stainless steel by chlorine gas or lead chloride in molten salts were also made.

Uranium dioxide was oxidized to U_3O_8 in remotely operable equipment to promote dissolution in the salt bath by reducing the particle size of the oxide. For 15-lb batches of UO_2 a flow rate of 2 liters of air per minute for 24 hours was sufficient to prepare feed for dissolution, although only partial oxidation to U_3O_8 was accomplished throughout the bed in this time. Sintering of the oxide during temperature excursions was a major problem.

Pilot plant operations were conducted in 20-liter and 80-liter fused silica crucibles with three salt systems: NaCl-KCl , $\text{PbCl}_2\text{-KCl}$, and LiCl-KCl . Primary purpose of the work in the NaCl-KCl salt system was to produce 100 lb of electrolytic UO_2 for evaluation as a fuel material, the dissolution of oxides was not studied. Electrolytic deposition of UO_2 from equimolar NaCl-KCl at 700 to 800 °C with uranyl chloride monohydrate feed was studied. Although no initial dissolution was required with this feed material, water remaining in the bath raised the oxygen-to-uranium ratio of the product and had to be removed by hydrogen chloride or chlorine gas sparging. Side reactions that produced U(IV) in solution and corrosion of graphite anodes were major operating problems in this system. Dual vessel operations were also evaluated.

The PbCl_2 -KCl system was operated at 600 to 700 °C, and dissolution of UO_3 and U_3O_8 was achieved by sparging the salt bath with chlorine through quartz tubes. A reference electrode system was necessary to control the cathode-to-melt potential to prevent lead metal deposition during electrolysis. A maximum size deposit of 116 lb of UO_2 was obtained in an 80 liter salt bath with Hastelloy D[®] cathodes. Disadvantages of this system were the high operating temperature, the volatilization of lead chloride that plugged off-gas lines, and the inability to remove small amounts of lead or lead chloride from the deposit.

The LiCl-KCl salt system was finally selected as the most suitable one. Although it is hygroscopic at room temperature, its use permits operation at only 500 to 600 °C, and consequently long lifetimes for the metal exposed to the chlorine atmosphere in the vapor space are achieved. Dissolution rates were improved in this system by chlorine sparging with a submerged gas lift. Improved atmosphere control techniques consistently resulted in oxygen-to-uranium ratios below 2.01, deposits exhibiting high densities, good crystal structure and chloride contents in the range 50 to 100 ppm.

Severe corrosion of metallic nickel-base cathodes beneath the deposit affected crystal structure, and porous graphite cathodes caused high carbon contamination of the product through mechanical interlocking. Hastelloy D cathodes were used in pilot plant runs in the PbCl_2 -KCl system with marginal corrosion rates, but corrosion rates were too great in the LiCl-KCl system. Platinum electrodes were severely corroded by chlorine at the salt-vapor interface, and interface protection devices proved unworkable. The cathode problem was finally solved by using graphite electrodes with impervious pyrolytic graphite coatings, which facilitated removal of the deposits from the electrodes and gave product carbon contents below 50 ppm.

Alternate container materials other than fused silica were evaluated. All metals corroded excessively, although nickel-aluminum alloys corroded least. Several types of graphite crucibles and susceptors were tested

[®] The Union Carbide Company

successfully with salt, but were rejected for use during codeposition because of the corrosion of graphite in oxygen and its ability to keep Pu(IV) from oxidizing. Other nonmetallic materials such as alumina offered no advantages over the brittle quartz.

Studies of the codeposition and partition steps, using cerium as a stand-in for plutonium, led to the conclusion that the oxygen-chlorine sparges necessary to oxidize plutonium to Pu(IV) during electrolysis were compatible with the production of deposits with good crystal structure and oxygen-to-uranium ratios below 2.01. Precipitation of PuO_2 was studied by using a cerium stand-in. Adherence of the oxide to the quartz crucible and to gas-lift recovery devices limited precipitate recoveries to less than 60%.

Integrated crushing, grinding and sieving devices to produce the three narrow particle size distributions desired for obtaining high densities by vibratory compaction were evaluated. The following series of devices was selected for hot cell use. The deposit is stripped from the electrode, and cut up into half-inch chunks with a hydraulic press. After the UO_2 is washed with water to remove the chloride salts, the -4 + 10 mesh and -35 + 65 mesh size fractions are made with a series of stepped parallel plates mounted in the press. Ball milling for 12 hours produced minus 200 mesh fines from the unwanted size fractions.

Chlorine and hydrogen chloride were removed from the off-gas by caustic scrubbers in all pilot plant operations. Continuous hydrogen peroxide additions to the caustic proved effective in destroying hypochlorite for subsequent storage of the caustic in stainless steel tanks. Recovery of chlorine and iodine entrapment from the off-gas by chlorine liquefaction at atmospheric pressure and -100 °C were also studied in the pilot plant.

DECLADDING

Studies of fuel element decladding for the Salt Cycle process were directed toward the following requirements: (1) a dry core for charging to the salt bath should be produced directly, (2) a minimum cladding waste volume should be produced, (3) the technique should be applicable to variable geometry fuel elements, and (4) decladding should not interfere chemically with

subsequent dissolution and electrolysis of the fuel material. Aqueous decladding techniques were not considered in the experimental studies. Three general types of decladding were briefly studied in laboratory-scale tests: (1) removal of the fuel from the cladding by mechanical vibration or oxidation of the UO_2 , (2) gas phase reactions of the cladding with chlorine or hydrogen chloride, and (3) dissolution of the cladding in molten salts by chlorine, hydrogen chloride or metal replacement reactions.

Mechanical decladding is applicable only to certain geometries but produces small quantities of wastes because the cladding is left as a compact metal. To provide an alternative for difficult fuel element geometries and for cladding that might be chemically bonded to the fuel, chemical decladding was also studied. Vibrational decladding was chosen for the hot cell demonstration, and gas phase decladding with nitrogen-diluted chlorine was developed as the backup chemical decladding technique.

Vibrational Decladding

In an initial test an 8-ft-long, 0.5-in.-diam, cold-swaged Plutonium Recycle Test Reactor (PRTR) fuel rod was fixed in a vertical position and UO_2 was vibrated out the lower end after the end plug had been removed with a tubing cutter. The UO_2 was easily removed using a small jack hammer as a vibrator. A second test was made with the same type of rod using an ultrasonic vibrator normally used for vibratory compaction of fuel elements. The UO_2 was not removed from the fuel element by this method with the ultrasonic coupling device available. It was concluded from these scouting studies that the UO_2 could be mechanically removed by a vibrational technique.

Since irradiated fuel might react with the cladding or sinter into a compact mass that would be difficult to vibrate loose, a test was conducted in the 327 Building Radiometallurgical Facility with a 2-ft-long by 0.5-in.-diam section of a vibrationally compacted 1200 MWd/ton fuel element irradiated in the PRTR. The section was held horizontally in a vise and a 5000-blow/min air hammer was held against it by a remote manipulator. The UO_2 flew out of the cladding during less than a minute's hammering, indicating that little sintering had occurred. Close visual examination of the cladding showed a clean, metallic surface on the inside of the cladding.

The initial success of vibrational decladding led to its selection as the primary remote decladding technique for removal of mixed oxide fuels from 19-rod clusters in the Salt Cycle demonstration.⁽⁷⁾ As shown in Figure 3, the developed decladder consisted of an air hammer with a speed up to 5000 blows/min, a vertical stationary anvil that supported the fuel rod full length, and a counterweighted, manually-movable air hammer carriage fastened to the anvil. The hammer and anvil were shaped to give six points of contact on the fuel rod circumference.

Successful tests were made on 0.5-in.-diam Zircaloy-clad fuel rod segments. The full length 8-ft fuel rods were bisected with a tubing cutter and placed against the anvil with the open end down into a tapered lower support containing a discharge into the oxide receiver. The lower support was equipped with a vacuum line to remove dust that might escape through the tapered fit during vibration. The upper support was then clamped over the fuel rod and cap by means of an air cylinder. As the vibratory hammer moved along the tube, the UO_2 loosened and dropped into the receiver.

The UO_2 was removed from vibratory-compacted fuel rods by vibrating only the bottom of the tube. Cold-swaged rods required only one pass with decladding times of about 2 min per half-rod, but a hot-swaged rod required 5 passes up and down the tube. The loading, decladding and unloading times were less than 10 min for any half-rod tested. The average losses of UO_2 to the cladding from 7 cold-swaged half-rods and 3 vibratory-compacted half-rods were 0.072% and 0.014%, respectively. These losses were measured by leaching the cladding with hot concentrated nitric acid and analyzing the aqueous solutions. The one hot-swaged rod tested gave an unexpectedly low waste loss of 0.013%.

One could tell that a half-rod was empty from the sound of the air hammer. Weighing the rod and comparing it with the estimated cladding weight was also useful. In remote operations the manipulator operator could easily tell if appreciable oxide remained in the rod by feeling the shift in its center of gravity, by weighing it, or by probing inside the tube with a ruler. The initial design of the remotely operable decladder provided for a calibrated wire to pass into the tube as the air hammer moved up the fuel rod. This

FIGURE 3
Vibratory Decladding Apparatus

proved to be mechanically cumbersome and was abandoned before it worked successfully.

The satisfactory performance of the vibratory decladding apparatus with irradiated fuel is reported elsewhere.⁽⁷⁾

Oxidative Decladding

One approach to the removal of the fuel from the cladding was a method similar to that developed by Atomics International⁽⁸⁾ for the Airox process in the re-enrichment of oxide fuels. The UO_2 is oxidized with air or oxygen to produce U_3O_8 which is less dense than UO_2 and expands, rupturing the cladding with the powder spilling out to a receiver.

A version of oxidative fuel-cladding separation was used by Benedict⁽⁹⁾ in the first laboratory scale Salt Cycle hot cell experiments. After the fuel rods were cut up into 1-in. lengths, they were placed on a coarse screen above the salt pot and air was passed through the screen. The U_3O_8 dropped through the screen into the salt pot as it formed.

Two oxidative core removals were attempted in a pilot plant reactor used for gas phase dissolution studies. The objective was to operate at a temperature and gas flow rate which would split the 35-mil-thick Zircaloy-2 cladding as the UO_2 oxidized to U_3O_8 and thus provide uniform removal of the core from long fuel elements. The first test element was a 3-ft-long, 0.5-in.-diam fuel pin with 2 rows of 0.125 in. holes diametrically opposed and spaced an inch apart. When exposed to air at 425 to 535 °C, the cladding bulged as is shown in Figure 4 but did not split and very little U_3O_8 was removed. In a second run, a 22-in.-long fuel pin was exposed to oxygen at 600 °C for 4 hr. Some oxidation occurred and the cladding bulged around the drilled holes. The run was continued at 720 °C for an hour, during which the cladding split in three places, providing considerable area for further oxidative attack.

Further development of the oxidative decladding approach for use in the Salt Cycle demonstration was discontinued when it became clear that the mechanical operations and time cycles involved compared unfavorably with vibrational decladding for the fuel elements to be used.

First Test at 425-535 °C for 6 Hours

Second Test at 600 °C for 4 Hours and at 720 °C for 1 Hour

FIGURE 4
Oxidative Decladding Test Results

Gas-Phase Chlorination of Zircaloy

Data on the gas phase chlorination and hydrochlorination of oxidized Zircaloy-2, using an alumina pellet bed for a heat transfer medium are summarized in Table I. A coupon of Zircaloy-2 was dissolved in chlorine gas in approximately 3 hr with the reaction starting at 400 °C and the temperature rising to as high as 800 °C. The chlorine flow rate had to be adjusted from 170 to 15 ml/min to hold the reaction in control. In a second run using hydrogen chloride gas, the reaction did not occur at 15 ml/min, but started and went smoothly at 55 ml/min. The temperature varied from 400 °C to a maximum of 480 °C, at which it remained constant. About 0.8 g of Zircaloy-2 was dissolved in 0.5 hr. The alumina pellets did not provide good heat transfer from the reaction zone because the bed could not be fluidized at the small gas flows used. The ZrCl_4 reaction product condensed out on the cold surfaces at the top of the reactor, which indicated the necessity for equipment designed to avoid plugging the reactor chamber. The sublimation temperature of ZrCl_4 is about 300 °C.

The chlorination or hydrochlorination of Zircaloy-2 without a heat transfer medium such as alumina is difficult because of the highly exothermic reaction. However, heat transfer media are not desirable with UO_2 cores because of the difficulty of separation of the core from the bed. Hence, mixing of the halogen gas with an inert gas was attempted to control the reaction. Chlorine was used exclusively in these studies to avoid the hydrogen production problem associated with the reaction of hydrogen chloride with zirconium.

Laboratory scouting studies made with coupons and small fuel pins to determine operable ratios of inert gas to chlorine are summarized in Table I. With the first fuel pin the UO_2 core was exposed in 2.5 hr but was not completely declad as shown in Figure 5. The reacting gas had an initial 4-to-1 nitrogen-to-chlorine ratio, which was gradually decreased to a 1-to-1 ratio during the run. The decladding was not completed because of vapor deposition of ZrCl_4 on the cooler areas of the element. In another decladding, the initial nitrogen-to-chlorine ratio was set at 1-to-1 and reduced to 1-to-2 after an hour. All of the cladding except a small part of one end plug was removed in

TABLE I
GAS-PHASE DECLADDING STUDIES

<u>Run No.</u>	<u>Feed Material</u>	<u>Geometry</u>	<u>Total Sample Weight, g</u>	<u>Furnace Temp, °C</u>	<u>Gas</u>	<u>Rate, ml/min</u>	<u>Time, hr</u>	<u>Remarks</u>
PL-1	Oxidized Zircaloy-2	3/4 in. tubing section in an alumina bed	2.1	400	Cl ₂	170 to 14	1.0	Formed ZrCl ₄ (white powdery layer on all cold surfaces above reaction bed). Produced considerable heat (up to 800 °C).
PL-2	Oxidized Zircaloy-2	3/4 in. tubing section in an alumina bed	2.0	400	HCl	14 to 56	0.5	0.8 g reacted forming ZrCl ₄ . Produced some heat (up to 480 °C).
GP-1	Zircaloy-2 clad UO ₂ fuel element	1/2 in. x 3-1/2 in. pin	90.5	420 to 590	Cl ₂ and N ₂	50 to 150 150 to 200	2.4	Fuel core was exposed and one end plug totally dissolved.
GP-2	Zircaloy-2 clad UO ₂ fuel element	1/2 in. x 3-1/2 in. pin	88.7	510 to 580	Cl ₂ and N ₂	150 to 300 150	2.5	Cladding was completely removed and only a part of the upper end plug remained. Gave off much ZrCl ₄ at 500 to 525 °C.
NPD-1	Zircaloy-2 clad PRTR fuel rod	1/2 in. x 36 in.	1226.	~ 400	Cl ₂ and N ₂	2000 2000	3.0	Wt loss = 65.9 g.
NPD-2	Zircaloy-2 clad PRTR fuel rod	1/2 in. x 36 in.	1177	~ 500	Cl ₂ and N ₂	1500 to 2000 1500	1.7	Wt loss = 60 g. Caustic scrubber blowback caused termination of this test. Inadequate vacuum to remove ZrCl ₄ .

14

BNWL-354

0 1 2 3
Inches

Run GP-1

$T = 420^{\circ}\text{C}$ to 590°C , $\text{N}_2/\text{Cl}_2 = 4/1$ to $1/1$, Time 2.5 hr

Run GP-2

$T = 415^{\circ}\text{C}$ to 645°C , $\text{N}_2/\text{Cl}_2 = 1/1$ to $1/2$, Time 2.5 hr

FIGURE 5

Gas-Phase Chlorination of Oxidized Zircaloy-2

2.5 hr. The starting temperature was 415 °C. The maximum temperatures observed during the first and second parts of the run were 535 °C and 645 °C, respectively.

Two chlorinations of Zircaloy-2 were made in a small pilot plant reactor (49-in.-long by 2.5-in.-diam) containing a 3-ft section of a 0.5-in.-diam PRTR fuel rod. In the first run 4 liters/min of a 1-to-1 nitrogen-to-chlorine ratio were used at temperatures between 425 and 575 °C. Approximately 33% (65 g) had been removed when the run was stopped in 30 min because of plugging of the off-gas line with ZrCl_4 . The second run was made with a gas preheater in the line ahead of the reactor, but was stopped by a scrubber blow-back after 30% of the cladding had been removed. In both runs the part of the ZrCl_4 condensed on the walls of the reaction vessel contained about 0.1 wt% uranium.

Decladding by Sparging Molten Salts

Decladding of Zircaloy-2 by sparging molten salts with halogen gases is summarized in Table II. Coupons of oxidized Zircaloy 35 mils thick, weighing from 2 to 2.5 g, were reacted with chlorine and hydrogen chloride using 30 g of equimolar NaCl-KCl molten salt as a heat and mass transfer medium. Complete dissolution of the Zircaloy-2 occurred at 800 °C with 240 ml/min hydrogen chloride flow in less than 2.5 hr. With 84 ml/min of HCl complete dissolution did not occur, but with a HCl sparge of 200 ml/min, the coupon dissolved in less than 1.5 hr. The rates of dissolution were evidently strongly influenced by the condition of the oxide film on the Zircaloy. In an experiment using 140 ml/min chlorine gas rather than hydrogen chloride, 1.3 g of Zircaloy-2 were dissolved in 1.7 hr indicating little change in dissolution rate with a change in reactant gas. In these experiments the ZrCl_4 reaction product was not volatilized but remained in the solid and black ZrO_2 was noted in the melts.

In an effort to speed the reaction of Zircaloy-2 with chlorine, 0.5 mol% CuCl was added to the initial NaCl-KCl melt. The coupon completely dissolved in 50 min at a chlorine flow of 170 ml/min. Doubling the catalyst concentration did not increase the dissolution rate.

TABLE II

DECLADDING BY GAS SPARGE IN MOLTEN SALTS

Salt System: 30 g of 50 mol% NaCl-50 mol% KCl
 Cladding: 3/4 in. diam section of oxidized Zircaloy-2 tubing
 Temperature: 800 °C

<u>Run No.</u>	<u>Sample Weight, g</u>	<u>Gas Rate, ml/min</u>	<u>Time, hr</u>	<u>Remarks</u>
<u>Hydrogen Chloride Gas Sparge</u>				
14-C	2	84	1.75	Zircaloy did not dissolve.
14-D	2	240	2.33	Tubing almost completely dissolved. Left some black crud in salt which appeared to be ZrO ₂ .
14-E	2.1	200	1.58	All dissolved except for some very fine particles.

Chlorine Gas Sparge with Cuprous Chloride Catalyst

<u>Run No.</u>	<u>Sample Weight, g</u>	<u>Weight CuCl, g</u>	<u>Gas Rate, ml/min</u>	<u>Time, hr</u>	<u>Remarks</u>
PL-3	1.5	0.22	170	0.92	All dissolved.
PL-3-C	2.2	0.22	149	0.50	1.6 g dissolved. Used 10 minute air sparge following Cl ₂ .
PL-10	2.2	0.44	149-0 spasmodic	~ 1.	Cl ₂ leak, experiment stopped. 1.4 g of the Zircaloy dissolved, turning salt black.
PL-10B	1.9	0.44	149	0.50	1.3 g of the Zircaloy dissolved Employed 10 min air sparge following chlorination.

17

BNWL-354

Metal Replacement Reaction

Scouting studies on the metal replacement reaction of Zircaloy-2 with PbCl_2 , which has been previously studied by Argonne National Laboratory in the development of the ARCO process,⁽¹⁰⁾ are summarized in Table III. Zircaloy coupons dissolved in a PbCl_2 bath in about 2 hr within a temperature range of 450 to 550 °C. The ZrCl_4 was evolved and the lead reaction product settled to the bottom of the reaction vessel.

An equivalent reaction time was observed in an equimolar PbCl_2 -KCl molten salt. The ZrCl_4 was retained in the melt, however. In an equimolar NaCl-KCl melt at 800 °C, a Zircaloy coupon was dissolved in 15 min using a stoichiometric quantity of PbCl_2 , leaving the ZrCl_4 reaction product in the melt. Doubling the amount of PbCl_2 did not appear to increase the reaction rate.

Effect of Decladding on Electrolytic UO_2 Deposition

In an attempt to integrate the decladding studies with the electrolytic recovery of UO_2 , a 3.5-in.-long fuel pin was declad in PbCl_2 at 550 °C by the metal replacement reaction, as shown in Table IV. KCl was then added to make an equimolar PbCl_2 -KCl melt. The UO_2 from the pin was dissolved and the lead from the decladding reaction regenerated with a chlorine sparge of 270 ml/min over a 4-hr period. Subsequent electrolysis at 500 °C provided only a small deposit of UO_2 and a very low current efficiency. Analysis of the melt showed that the lead had not been completely regenerated, perhaps accounting for the poor electrolysis.

Further electrolysis tests with melts containing Zircaloy as an impurity indicated that the retention of dissolved cladding in the salt is not desirable. For example, in a melt of 53 mol% PbCl_2 - 47 mol% KCl containing 2.5 wt% dissolved zirconium, only a small deposit of low-grade UO_2 crystals was obtained, while in a similar melt without zirconium present a good deposit of UO_2 was obtained. Zircaloy appeared to have little effect on electrolyses in a NaCl-KCl melt. However, even in that system there is still an incentive for cladding removal before charging feed to the salt melt because the buildup of high concentrations of ZrCl_4 in the bath would result in ZrCl_4 volatilization.

TABLE III

DECLADDING WITH METAL REPLACEMENT REACTION

<u>Run No.</u>	<u>Sample Weight, g</u>	<u>Salt System</u>	<u>Temp, °C</u>	<u>Remarks</u>
<u>Feed: UO₂ Fines</u>				
PL-6	3.0	53 mol% PbCl ₂ 47 mol% KCl 61 g Pb	550	Most did not dissolve. > 95% of the U found in interface layer.
PL-7	3.0	60 g PbCl ₂ 82 g Pb	550	Most did not dissolve. > 95% of the U found in interface layer.
<u>Feed: 3/4 inch diam section of oxidized Zircaloy</u>				
PL-4	1.9	60 g PbCl ₂	450	All dissolved producing heat (up to 550 °C). 81% volatilized, lead was left in bottom portion of melt.
PL-5	2.2	53 mol% PbCl ₂ 47 mol% KCl	450	All dissolved and stayed in solution. Produced heat (up to 550 °C).
PL-11	2.2	25.2 g PbCl ₂ 14.8 g KCl-NaCl	500	Used 100% excess PbCl ₂ . Rapid re-action when Zr dropped into salt and no ZrCl ₄ was given off. All dissolved.
PL-11-B	2.0	12.5 g PbCl ₂ 20 g KCl-NaCl	700	Used stoichiometric amount of PbCl ₂ . Zr turned red when dropped in 700 °C salt and gave off gas bubbles which were absorbed in solution. All dissolved, no volatilization.

TABLE IV
EFFECT OF DECLADDING ON ELECTROLYTIC UO₂ DEPOSITION

<u>Run No.</u>	<u>Feed Material</u>	<u>Geometry</u>	<u>Sample Weight, g</u>	<u>Salt System</u>	<u>Temp, °C</u>	<u>Chlorine Gas Rate ml/min</u>	<u>Sparge Time, hr</u>	<u>Remarks</u>
PL-15	UO ₂ fuel element	1/2" x 3-1/2" pin	34.9 Zr 52.9 UO ₂	PbCl ₂ 1750 g	600	270	2.5	Zr dissolved, ZrCl ₄ volatilized. Added enough KCl to obtain 53 mol% PbCl ₂ - 47 mol% KCl, added 7.5 g of CuCl as catalyst and electrolyzed (poor electrolysis product).
PL-16	UO ₂	200 mesh	100	53 mol% PbCl ₂ 47 mol% KCl 1500 g CuCl 3 g	550	150	2.5	Electrolysis - poor deposit. Experiment terminated by cracked crucible.
PL-18	UO ₂ Cl ₂ ·H ₂ O	Soluble Salt	140	53 mol% PbCl ₂ 47 mol% KCl 2.5 g Zr Total 1592.5 g	550	150	3.0	Very small, poor deposit. Poorly adherent to electrode. 1.5 V during 1 hr electrolysis.
PL-18B	UO ₂ Cl ₂ ·H ₂ O	Soluble Salt	140	53 mol% PbCl ₂ 47 mol% KCl Total 1500 g	550	150	2.25	Duplicate of PL-18 without Zr present. Much larger deposit than in PL-18. 1 hr electrolysis at 1.5 V.
PL-21	UO ₂ Cl ₂ ·H ₂ O	Soluble Salt	70	50 mol% KCl 50 mol% NaCl 2.4 g Zr Total 702.4 g	800	150	2.3	Fair deposit on cathode. There was an undissolved piece of Zr in the bottom of the bath that had a like deposit of UO ₂ on it. (~ 1 hr electrolysis at 1.5 V).
PL-21B	UO ₂ Cl ₂ ·H ₂ O	Soluble Salt	70	50 mol% KCl 50 mol% NaCl 5 g TlCl 2.2 g Zr Total 707.2 g	800	150	2.5	Good deposit with good crystal structure. (1.5 hr electrolysis at ~ 1.5 V).
PL-23	UO ₂ Cl ₂ ·H ₂ O	Soluble Salt	140	50 mol% PbCl ₂	600	150	3.0	Fair deposit. (0.58 hr electrolysis at 1.5 V)
PL-28	UO ₂ fuel element	1/2" x 3-1/2" pin	36 Zr 53.7 UO ₂	70 mol% KCl 30 mol% PbCl ₂ 10 g Total 150 g	500	270	3.5	Gave off copious quantity of ZrCl ₄ during dissolution. Very small deposit on cathode - mostly near interface. (1.5 hr electrolysis at 1.5 V)

Chlorination of Stainless Steel

Information from work at Brookhaven National Laboratory^(11,12) indicated that gas phase chlorination of stainless steel required higher temperatures than for Zircaloy (above 600 °C) and had a greater tendency toward an uncontrollable reaction. Therefore dissolution by chlorine was studied only with molten salts as heat transfer media. The results generally confirmed the high temperature requirements for stainless steel dissolution found at the other sites.

The dissolution tests using 35-mil-thick, 2.5 g coupons of 316 stainless steel are summarized in Table V. A stainless steel coupon lost 1.1 g in 30 min in a NaCl-KCl melt with 0.5 mol% CuCl catalyst at 750 °C. In a control test, a coupon was not significantly attacked in the absence of the CuCl catalyst. A stainless steel coupon did not dissolve in PbCl₂ at 500 °C by the metal replacement reaction alone but dissolved in about 40 min with the evolution of brown fumes when 150 ml/min of chlorine was sparged through the melt. Stainless steel did not dissolve in a NaCl-KCl melt at 800 °C by the metal replacement reaction with PbCl₂. This lack of success is in agreement with thermodynamic calculations based on the pure substances.

OXIDATION

The oxidation of UO₂ to U₃O₈ is performed in the Salt Cycle process to increase the reactivity of the oxide in the subsequent dissolution with chlorine in the molten salt bath. Although U₃O₈ does dissolve an order of magnitude more rapidly than UO₂ with the same particle size,⁽¹³⁾ the increased rate of dissolution of oxidized material is due primarily to the increase in surface area of the solid, caused by the fracturing of the solid as it is converted to less dense U₃O₈. Another result of oxidation which probably has a beneficial effect on dissolution is the greater ease of suspension of the smaller particles during stirring by the chlorine gas. The inclusion of several air-oxidation hydrogen-reduction cycles on the oxide is also believed to increase the reactivity of the oxide, presumably by further reducing the particle size and by creating active sites for dissolution.^(7,8)

TABLE V
DECLADDING OF STAINLESS STEEL

Feed: Section of 3/8 inch diam 316 Stainless Steel Tubing.

<u>Run No.</u>	<u>Sample Weight, g</u>	<u>Salt Composition</u>	<u>Temp, °C</u>	<u>Chlorine Gas Rate, ml/min</u>	<u>Sparge Time, hr</u>	<u>Remarks</u>
PL-12	2.5	50 mol% KCl 50 mol% NaCl 0.32 g CuCl catalyst 30 g	750	149	0.50	1.1 g dissolved, the remaining was gray in color and easily crumbled after drying.
PL-12B	2.2	50 mol% KCl 50 mol% NaCl 30 g	750	149	0.50	0.2 g weight loss. Showed no sign of attack.
PL-13	2.4	PbCl ₂ 40 g	600	0	---	0.1 g weight loss. No visible sign of attack.
PL-13B	2.3	PbCl ₂ 40 g	600	149	0.50	Dissolved completely. Released dark brown smoke during dissolution.
PL-14	2.2	25 g PbCl ₂ 20 g KCl-NaCl	650	0	---	No reaction, salt turned brown.
PL-14B	2.0	12.5 g PbCl ₂ 20 g KCl-NaCl	650	0	---	No reaction.

22

BNWL-354

For the bulk of the cold pilot plant work, it was sufficient to place the UO_2 in metal trays in an oven with an air atmosphere. The UO_2 was totally converted to U_3O_8 after standing overnight at 400 to 500 °C. For example, the feed materials for Runs-LK 26, 28 and 29 in the LiCl-KCl pilot plant electrolyses had O/U ratios of 2.664 and 2.668 after such treatment. Temperatures above 600 °C caused sintering and temperatures below 400 °C resulted in incomplete conversion of the oxide.

For remote operations, the apparatus shown in Figure 6 was designed to permit oxidation and dumping of the oxide into the salt bath. The objectives of the remote equipment were to couple the oxidizer directly to the decladder, to get enough oxygen to the UO_2 to oxidize it in a reasonable time interval without fluidizing the fines out of the bed, to contact all the UO_2 with the oxygen, to control the reaction rate to prevent runaway reactions that would cause sintering, to be able to pour out all or part of the oxide, and to minimize radioactive dust in the cell atmosphere.

Typical oxidation runs made during the testing of the equipment with 30-lb batches of minus 3 mesh fused UO_2 powder are shown in Table VI. A 30-lb batch is approximately double the average batch size used in the Salt Cycle Demonstration.⁽⁷⁾ Only a partial oxidation was considered sufficient since the primary purpose of the oxidation is not to produce U_3O_8 , but to break up the UO_2 particles. The weight change was used to indicate the approximate degree of oxidation. The least desirable occurrence during oxidation was a temperature excursion above 600 °C that sintered the oxide and made it difficult to pour. High gas flow rates (5 liters/min) fluidized the finely divided product in the oxidizer and reduced the degree of oxidation by cooling the packed bed of UO_2 , although the inlet gas had been preheated by entering in a line that passed through the bed. Redesign of the container was necessary before the oxide could readily be poured. The final design included a rotating ring about 3-in. diam in the throat of the nonsymmetrical taper to break up partially sintered oxide. Appreciable variation in the degree of oxidation throughout the bed was encountered even when all the UO_2 feed had been converted to a fine powder. However, since complete oxidation was not required for dissolution, it was not felt necessary to improve the

FIGURE 6
Remote Oxidizing Equipment

TABLE VI
OXIDATION OF UO₂ IN PROTOTYPE OXIDATION EQUIPMENT

Feed Material: 30 lb of minus 3 mesh arc fused UO₂

Run No.	Vol% O ₂ in Gas	Gas Flow		Temp, °C	Ratio of O ₂ Used to Stoic. O ₂	Wt Gain, lb	Final O/U Ratio	Percent Oxidized		Comments
		Rate, l/min	Time, hr					from Wt. Gain	from O/U Ratio	
OX-R1	Air	1.5	23.5	450	1.2	1.05	---	89	---	
OX-1	42-58	1.4	23.0	350-520	1.9	1.2	2.664	101	99.6	Bed volume in- creased by 230%.
OX-2	40-50	1.4	21.8	330-400	2.2	1.1	---	93	---	No temperature excursions.
OX-3A	26	2.7	21.0	400-500	2.3	1.0	---	84	---	Excursions to 675 °C.
OX-5	Air	5.0	28.3	440-480	4.4	0.8	2.432	67	64.8	Unoxidized UO ₂ present in the poured powder.
OX-6	Air	2.5	26.8	570	2.2	0.95	2.649 High Value* 2.209 Low Value*	80	97.3 31.3	All parts of the bed apparently partially oxi- dized.

*Several samples taken throughout bed.

25

BWT-351

apparatus. The percentage of oxygen in the feed was a compromise between the time necessary to pass a stoichiometric quantity of oxygen through the bed and the ability to control the reaction. A flow rate of 2 liters/min of air at 500 °C for 24 hr for a 15-lb batch of oxide feed was finally selected as a compromise for the Salt Cyce demonstration.^(7,14)

SALT SYSTEM PROPERTIES

Three salt systems were used in pilot plant operations: NaCl-KCl, PbCl₂-KCl, and LiCl-KCl. Operation at the lowest possible temperature was desired in order to reduce corrosion of metallic parts of the off-gas system by chlorine gas, corrosion of potential metallic candidates for containers and electrodes, and corrosion of graphite electrodes by air or chlorine.

Phase Diagrams

Phase diagrams of the three salt solvents are shown in Figure 7.⁽¹⁵⁾ The NaCl-KCl system has a minimum melting solid solution near equimolar NaCl-KCl, which melts at about 660 °C. The minimum operating temperature below which freezing problems occurred in the pilot plant was about 700 °C. Although the vapor pressures of NaCl and KCl are below 0.1 torr in this region, small quantities of solids were found in the off-gas piping. These solids would have to be removed during extended operating periods. Determination of the liquidus curve by differential thermal analysis for equimolar NaCl-KCl gave a monotonic decrease in melting point with added UO₂Cl₂ from 660 °C to 490 °C at 41 mol% UO₂Cl₂.⁽¹⁶⁾ Measurements at higher uranium concentrations were prevented by the thermal decomposition of UO₂Cl₂.

The KCl-PbCl₂ phase diagram is more complex because of compound formation. At the 2.5 KCl-1 PbCl₂ mole-ratio composition at which pilot plant operations were conducted to prevent electrodeposition of lead, KCl freezes out at about 570 °C. Addition of UO₂Cl₂ to 2.5 KCl-1 PbCl₂ significantly lowers the freezing point as is shown in Figure 8.⁽¹⁶⁾ A concentration of 30 wt% UO₂Cl₂, which was achieved in pilot plant runs, lowers the melting point to 415 °C, but electrolyzing out the uranium again raises the melting point so that the pure solvent composition controls the operating temperature. Pilot

FIGURE 7
Phase Diagrams of Molten Salt Solvents

FIGURE 8
Phase Diagram for KCl-PbCl₂-UO₂Cl₂

plant electrolyses were conducted at 600 °C and uranium oxide dissolutions as high as 700 °C. The vapor pressure of PbCl_2 is 0.1-1.0 torr in this region, and plugging of the 4-in. off-gas line with PbCl_2 dust occurred frequently during extended pilot plant runs.

The LiCl-KCl system forms a simple eutectic at 40 mol% LiCl that melts at 340 °C. Operations with this system were conducted with a solvent of 53 mol% LiCl for codeposition and 72 mol% LiCl for partition of UO_2 from Pu(III) . The addition of UO_2Cl_2 first decreases and then increases the melting point as is shown in Figure 9.⁽¹⁶⁾ The operating range of 500 to 600 °C was determined not by the melting point of the salts but by the achievement of practical rates of dissolution of U_3O_8 and current densities during electrolysis governed by the resistance of the salt bath. The hygroscopic nature of LiCl required that it be kept sealed or in a dry atmosphere at all times when at room temperature. Reduction of the relative humidity from the normal 35% to 10% was often enough to reduce moisture pickup to acceptable levels for handling frozen salt.

Densities of Molten Salts

The density of the molten salt is useful in sizing equipment and in determining the uranium content. Densities of PbCl_2 -2.5 KCl (the only system for which appreciable data are available) with added UO_2Cl_2 are shown in Figure 10 as a function of temperature.⁽¹⁷⁾ The PbCl_2 -2.5 KCl is not a sensitive system for uranium concentration measurement because of the high density of lead. The equimolar LiCl-KCl system, which varies in density from 1.6 to 2.1 g/cm^3 as the uranium content is increased from 0 to 10 wt%, was suitable for such measurement.

Electrical Conductivity of UO_2

The electrical conductivity of a sample of electrolytic UO_2 deposited from equimolar NaCl-KCl at 700 °C was measured by Battelle Memorial Institute (Columbus) using techniques reported in BMI-1135.⁽¹⁸⁾ The electrical conductivities shown in Figure 11 were measured on the first heatup of a sample UO_2 having an O/U ratio of 2.015. Presumably, the phase present is UO_{2+x} and in the low temperature region it behaves as a metal-deficient, or oxygen-rich

FIGURE 9
Phase Diagram for KCl-LiCl-UO₂Cl₂

FIGURE 10
Density of PbCl_2 -2.5 KCl with Added UO_2Cl_2

FIGURE 11
Electrical Conductivity of Electrolytic UO_2 Deposited from Equimolar NaCl-KCl at 700°C

semiconductor with a transition to electronic conduction at 500 to 600 °C. In BMI-1135 the electrical conductivity of UO_2 is shown to vary widely with the crystal structure and the thermal history and to decrease rapidly as the O/U ratio approaches 2. The conductivity of electrolytic UO_2 is comparable with that of the sintered UO_2 discussed in that report and of single crystals of UO_2 .⁽¹⁹⁾

Very high voltage drops across the deposit were calculated from data presented in Figure 11 for a 0.5-in.-thick deposit with a current density of 0.5 amp/in.², typical conditions during pilot plant runs. Although the voltage drop is only 0.5 V at 700 °C at which the deposit was produced, voltage drops of 3.3 V at 600 °C and 20 V at 500 °C were estimated. However, the actual experience with pilot plant electrolyses that produced dense sheets of UO_2 at 550 to 600 °C indicated the drop across the deposit was only a very minor part of the total cell resistance, being at most only a few tenths of a volt. This apparent inconsistency can only be resolved by comparison measurements of resistances of UO_2 in salt baths and of products from the LiCl-KCl and $\text{PbCl}_2\text{-KCl}$ systems. Attempts to further lower the operating temperatures of the Salt Cycle process may run into the problem of high deposit resistances, which could result in deterioration of crystal structure and a practical limit on obtainable deposit thickness.

Decomposition Potentials of UO_2Cl_2 and Salt Solvents

In the alkali chloride solvents, the salt decomposition potentials are well above 2 V, so that high current densities in the deposition of UO_2 can easily be obtained without alkali metal deposition. In the $\text{PbCl}_2\text{-KCl}$ system, however, the codeposition of lead is a major problem. In order to eliminate the variable voltage drops at the anode, caused by the chlorine liberation that changes with current density, all potentials are measured with Ag/1 molal AgCl in $\text{PbCl}_2\text{-2 KCl}$ as the other half cell. The potential of such cells is shown in Figure 12 for lead in $\text{PbCl}_2\text{-KCl}$ mixtures and for 10 mol% UO_2Cl_2 in $\text{PbCl}_2\text{-KCl}$ mixtures. The gap between the UO_2^{++} and Pb^{++} reduction curves and the Pb^{++} allows operation at relatively high current densities if close control is maintained. The cell potentials are relatively weak functions of the salt composition and the operating temperature.

FIGURE 12
 Decomposition Potentials in PbCl₂-KCl-UO₂Cl₂ System

SODIUM CHLORIDE-POTASSIUM CHLORIDE PILOT PLANT OPERATIONS

Pilot plant electrolyses in the NaCl-KCl system were conducted in a fused silica crucible containing about 20 liters of molten salt. The salt was heated in a 13 kW Trent* furnace with Nichrome[®] heating elements. The apparatus is illustrated in Figure 13. Reactor-grade graphite electrodes were used throughout. The preferred electrode orientation was two anodes with one cathode in the center. The off-gas system consisted of a Transite[®] cover with a side arm discharging to a caustic scrubber. Equimolar NaCl-KCl was used as the solvent in all runs. The minimum operating temperature was 700 °C because of the high (650 °C) melting point of the solvent. A chlorine blanket over the melt was relied upon to keep air from the melt and there was no special attempt to exclude air from the vapor space. The major purposes of this series of runs were to produce 100 pounds of electrolytic UO₂ for evaluation by the Ceramic Fuels Development Operation and to determine the problems involved in operating the molten salt system in equipment suitable for large scale operation.

Dissolution and Drying

Because prolonged sparging of the molten salt with chlorine was believed to be necessary to totally dissolve uranium oxides and efficient gas sparging equipment had not yet been developed, uranyl chloride monohydrate (UO₂Cl₂·H₂O) was selected as a starting material since it would readily dissolve and would require a minimum of gas sparging for drying. Commercially available UO₂Cl₂·H₂O was introduced into equimolar NaCl-KCl at 700 °C. Water evolved from the system, accompanied by splattering and bubbling. Nevertheless, about one pound of UO₂Cl₂·H₂O could safely be added per minute at a continuous rate of addition. Evolved hydrogen chloride from the decomposition was detected both by odor and by the presence of an acid in the off-gas. Subsequent analysis of samples of the frozen salt with Karl Fischer reagent indicated that as much as 0.75 moles of water per mole of UO₂Cl₂ was still present in the salt at 700 °C. Improvements in moisture control during sampling reduced

* Trent, Inc., Philadelphia, Pa.

® Driver-Harris Company

® Johns-Manville Company

Salt Bath Assembly

Electrolysis Apparatus

FIGURE 13
Pilot Plant Equipment for Production of Electrolytic UO_2 in Equimolar NaCl-KCl

the indicated moisture in the sample but showed that at least a third of the water in the monohydrate is still present in some form in the molten salt bath. This result emphasizes the difficulty in removing moisture from molten salt baths. It is unlikely that the water is present in these systems in its uncombined molecular form. It is probably present in hydrolyzed uranium species such as $\text{UO}_2(\text{OH})\text{Cl}$ or $\text{H}_2\text{U}_2\text{O}_7$. Direct electrolysis of the salt bath with reactor-grade electrodes at 700°C gave oxygen-to-uranium ratios of about 2.2. The high O/U ratio may have resulted from the reduction of UO_2Cl , $\text{U}_3\text{O}_8\text{Cl}$, or hydrolyzed uranium species to U_2O_5 , U_3O_8 , and U_4O_9 , producing a nonstoichiometric UO_2 deposit. The thermal decomposition of UO_2Cl_2 to U_3O_8 on the cathode may also have been a contributing factor.

Electrolysis

Three pilot plant runs are summarized in Table VII. Drying of the bath with chlorine gas reduced the product oxygen-to-uranium ratio below 2.02. Each electrolysis was accompanied by the buildup of U(IV) produced by both the reaction of U(VI) with the carbon anodes and chlorine gas, and the redissolution of UO_2 by chlorine at the cathode. The latter reaction is shown by the reduced current efficiency calculated from the weight of the product UO_2 . It probably contributed significantly to the reduction of the O/U ratio of the product. Because U(IV) will not deposit at the cathode, it was allowed to oxidize by standing in air overnight. The uranium content of the bath was not raised above 10 wt% because of the fear that thermal decomposition of UO_2Cl_2 might increase the O/U ratio of the product. This possibility was never quantitatively defined, although thermal decomposition to U_3O_8 had previously limited phase diagram determinations in this system to low uranium concentrations.⁽¹⁶⁾ An attempt at removal of the last bit of uranium from the bath immediately following the second run resulted in a high O/U ratio in the product (probably from air inleakage) and an increased current efficiency because of the decreased chlorine production at the anode.

Dual Vessel Experiments

A combination of two induction-heated 20-liter fused silica vessels was employed in experiments to increase the capacity of the system. The experiments are summarized in Table VII. Twenty pounds of UO_3 were dissolved

TABLE VII
PILOT PLANT ELECTROLYSES
Equimolar NaCl - KCl Salt System

Container: 20 liter, 9 inch diam fused silica crucible
Approximate Salt Weight: 65 lb
Feed Material: $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$
Electrode Material: Reactor Grade Graphite,
3/4 inch x 4 inch x 17 inch length submerged in salt

CHLORINE GAS DRYING			WT% URANIUM			ELECTROLYSIS							PRODUCT	
Run No.	Rate, l/min	Time, hr	Before	After		Temp, °C	Time, hr	Cell Voltage, V	Current Density, amp/in ²		Current Efficiency	Number of Anodes	Oxygen-to	Carbon
			Electrolysis	U Total	U(IV)				Initial	Final			Uranium Ratio	Content, ppm
NPL-1	1.82 to 0.65	3.9	9.9	6.8	1.2	730-735	2.8	1.70	3.24	2.06	67.2	1	2.012	1800
NPL-2	1.82	1.5	6.6*	3.1	0.7	730-735	4.0	1.40	1.85	1.11	66.1	1	2.019	580
NPL-3	----	0	3.1*	(1.2)	----	735-740	5.0	1.08	1.39	0.56	79.0	2	2.073	490
<u>Dual Vessel Experiments</u>														
NPL-4	Intermittent Mixing, See Figure 17**					700-715	----	1.55	2.78	1.30	65.2	2	2.011	3230
NPL-5	Continuous Mixing, See Figure 18**					705	----	1.64	2.26	1.30	66.0	2	2.106	640

*Destroyed U(IV) from previous run by allowing to stand overnight.

**20 lb UO_3 feed dissolved in each crucible.

in each vessel, and the electrolysis was conducted in one vessel until the bath was depleted in uranium as shown in Figure 14. The vessels were connected by two 3/4-in.-diam uninsulated quartz gas lifts. Chlorine gas at 2.5 liters/min was introduced in the gas lift discharging to the electrolysis cell and air at 2.5 liters/min was introduced into the gas lift moving salt from the electrolysis cell to the other vessel. The salt was recirculated between the vessels for 20 min. The electrolysis was then restarted with the same cathode as used before. A deposit with an O/U ratio of 2.011 and with about twice the weight of the average single vessel run was produced. The successful mechanical operation of the gas lift without freezing of the salt and with automatic self-regulation of the liquid levels in each vessel indicated the feasibility of producing large deposits of UO_2 by dissolving oxide or destroying U(IV) in one vessel and electrolyzing in the other with intermittent recirculation of the salt.

A second experiment to demonstrate continuous recirculation is shown in Table VII and Figure 15. The insertion of the cold electrodes into the bath lowered the temperature appreciably in the electrolysis cell. Consequently the degree of mixing during recirculation could be followed by the temperatures of the two baths. Electrolysis and recirculation were conducted simultaneously with identical gas lift operation as in the preceding run. A small quantity of UO_3 was purposely left in the second vessel to simulate continuous dissolution and recirculation. The high O/U ratio of 2.1 for the product indicates that the presence of undissolved UO_3 or U_3O_8 in the bath prevents the electro-deposition of stoichiometric UO_2 and that a two vessel dissolver-electrolysis system cannot be operated with simple continuous recirculation. The possibility of dissolving UO_2 directly in such a system still exists. However a filter in the gas lift would be necessary to keep UO_2 from settling into the electrolysis cell.

Evaluation of Electrolytic UO_2 Product

About 120 lb of UO_2 was produced in 35 runs in the NaCl-KCl salt bath shown in Figure 13. The deposit characteristics were relatively uniform along the electrode except at the surface of the melt, where the deposit tended to be more porous, contained more impurities and had a higher oxygen-to-uranium ratio.

FIGURE 14
Electrolysis with Intermittent Recirculation

FIGURE 15
Electrolysis with Continuous Recirculation

As shown in Figure 16, the crystal structure varied significantly from the inside of the deposit to the outside with the largest crystals being the last produced. The carbon content was highest next to the electrode, probably because of breaking away of graphite from the electrode during deposit removal.

A comparison of the particle size distribution of the washed and sieved products is shown in Figure 17. The cohesiveness of the deposit varied with the O/U ratio and the batch size of the run; high O/U ratios and thin deposits caused small, single crystals while low O/U ratios and thick deposits broke up with difficulty, and then only into large agglomerates.

The screen fractions for the primary and agglomerated particles of low U/O ratio deposits are shown in Figures 18a and 18b. These correspond to the two peaks in the particle size distribution shown in Figure 17. The product with high O/U ratios varied widely, ranging from the small, needle-like non-cohesive crystals shown in Figure 18c that are not suitable for fuel element fabrication to the large, well-formed crystals shown in Figure 18d that could be hydrogen-reduced to produce large, dense fuel particles. The more cohesive deposits were probably produced when there was some redissolution of UO_2 during electrolysis, which kept a smooth crystal face that continuously grew thicker rather than producing single crystals with void formation between them.

The results of laboratory analyses of the product are shown in Table VIII, which is based on 32 electrolysis runs. The specifications listed

TABLE VIII
CHEMICAL ANALYSES OF ELECTROLYTIC UO_2 PRODUCED
FROM THE NaCl-KCl SYSTEM

	<u>O/U</u> <u>Ratio</u>	<u>Carbon</u> <u>ppm</u>	<u>Chlorine</u> <u>ppm</u>	<u>Sodium</u> <u>ppm</u>	<u>Potassium</u> <u>ppm</u>
Median Value	2.016	1290	40	130	98
Specifications	<2.02	<100	<100	<100	<100

are those for UO_2 for PRTR fuels.^(20,21) Only the median values are reported here because of the wide variation in results caused by nonrepresentative

Oxygen to Uranium Ratio = 2.015

Side Next to Electrode

Cross Section

Growing Surface

0.10"

FIGURE 16
 UO_2 Deposit from NaCl-KCl Salt Bath

FIGURE 17
Effect of Agglomeration on Screen Analysis of Electrolytic UO_2

Run SCL-52 -35+45 Mesh,
O/U = 2.016

Run SCL-56 -6+10 Mesh,
O/U = 2.007

0.10"

Run SCL-61, Unscreened,
O/U = 2.038

Run SCL-65, Unscreened,
O/U = 2.062

FIGURE 18
Crystal Characteristics of UO_2 Deposited from NaCl-KCl

grab sampling, inaccuracy of analytical techniques which had not been perfected for low concentration ranges of impurities, and planned changes in operating conditions that were tried to obtain better products. The sodium, potassium, and chlorine contents of the product varied randomly, being neither a function of the O/U ratio or the crystal structure of the deposit. The sodium- and potassium-to-chloride ratios were consistently higher than if NaCl or KCl were occluded in the deposit, probably because of low chloride analytical results.

The carbon content of the deposit had a median value of 3100 ppm. This value cannot be tolerated in nuclear fuels because of carbide formation with the fuel and cladding and the possibility of gas evolution. Two major sources of carbon contamination were found. Corrosion of the graphite anodes and cathodes by air above the bath surface produces a fine graphite powder which falls into the bath, permeates the entire system and is eventually incorporated in the deposit. Graphite also adheres to the surface of the deposit when it is mechanically removed from the electrode.

The graphite concentration found in the fines of a screened deposit was 5 to 10 times greater than that in larger size particles. Either the particle size of the graphite or graphite-bearing UO_2 was originally small or abrasion during screening occurred. However, most of the graphite is not distributed throughout the interior of the particles. Separation of the graphite from the UO_2 by kerosene was attempted, but the UO_2 collected at the kerosene-water interface and part of it was present in both phases.

The oxygen-to-uranium ratio was apparently determined primarily by the wetness of the melt and the atmosphere. Poor atmosphere control was inherent in the apparatus, since an air sweep was passing over the bath surface to cool the Transite lid. The gas pretreatment of the melt is a strong factor in determining the O/U ratio of the product. Individual runs with each feed material showed that O/U ratios below 2.01 can be obtained with UO_2 , $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$, or U_3O_8 feeds with a controlled-atmosphere system and suitable sparge times.

EQUIPMENT FOR PILOT PLANT OPERATIONS

An induction-heated, fused silica electrolytic UO_2 pilot plant was constructed after completion of most of the NaCl-KCl studies. The NaCl-KCl operations reported in Table VII, the PbCl_2 -KCl pilot plant operations, and the 80-liter LiCl-KCl operations were conducted in the new apparatus.

Electrolytic Cell

The design of the electrolytic cell crucible and secondary container used in pilot plant operations is illustrated in Figure 19. The necessity for using fused silica because of corrosion to metals dictated a simple pot for the melt crucible. The fragile nature of the pot in turn, imposed limitations on the design of the secondary containers and lids for containing the chlorine and hydrogen chloride. Since the secondary container was also to be used as an induction-heating susceptor, additional geometric considerations were involved.

Two sizes of electrolytic cell crucibles were used in the pilot scale tests. These were 9-in.-diam, 30-in.-high and 18-in.-diam, 30-in.-high fused silica pipes with one end closed by fusion. The fused ends were hemispherical, providing a good geometry for dissolution operations and a mechanically strong base.

The secondary containers for the crucibles were metal cylinders with bottoms welded in place designed to provide a stable footing and a simple geometry for use as a susceptor with an induction heating coil. Rims were welded to the top to mate with the drybox or double chamber lids.

In the early studies with the smaller crucibles, a Transite lid with side arm connected to an off-gas vacuum system was used. A slotted top provided access for dissolution and electrolysis equipment. This design allowed some air to sweep over the top of the melt.

The lid design for the large crucibles was originally the same as for the 9-in. pots but difficulty was encountered in obtaining an air-free atmosphere over the melt because of poor sealing at the mating surfaces. A double lid was developed to provide an air-free lower chamber above the melt and an upper chamber with an exhaust for chlorine to an off-gas scrubber.

FIGURE 19
Eighty Liter Pilot Plant Salt Bath for PbCl_2 -KCl System

The lid mated with the susceptor through a quartz wool seal. A Hastelloy C[®] plate separated the lower melt chamber from the upper off-gas removal chamber. Holes in the plate provided access for process equipment such as electrodes, spargers, and thermowells. Electrodes were gasketed with Lavite[®] plates to minimize air access to the melt atmosphere.

A caustic tower removed chlorine from the off-gases. An 8-ft section of the 12-in.-diam column was packed with stainless steel Raschig rings. The off-gases were drawn through the tower with a 150 cfm capacity jet. The tower, associated piping and feed tanks were made of stainless steel. However, stainless steel is not a satisfactory material for a chlorine scrubber and frequent replacement of pumps and lines was necessary.

Two major pieces of electrical equipment were used with the electrolysis cell. An automatic control rectifier with a 500-amp 12-volt output was used in the electrolysis studies. It was modified to incorporate an optional reference electrode control system. A 10-kc 30-kW motor generator set was used for induction heating of the electrolysis cell. The salt temperature was controlled by on-off control with automatic switching to four power levels.

Auxiliary equipment consisted of gas lift recirculators, sparge tubes, thermocouple shields, vacuum transfer lines, and a waste salt receiving container with an especially designed lid for vacuum transfer. The gas lift recirculators were quartz tubes of varying sizes and shapes to which plastic gas supply tubes were attached. Quartz tubes were used for vacuum transfer lines with sparge tubes and thermocouple sheaths. The hot salt waste receiver was a stainless steel cylindrical tank with a lid equipped with a ball joint socket and a vacuum line. A silicone rubber gasket provided a vacuum-tight seal between the receiver and the lid. Stainless steel was used for the receiver tank because the short exposure to the molten salt before freezing produced little corrosion.

[®] Union Carbide Company

[®] D. M. Steward Mfg. Co.

Instrumentation

The instrument systems used in the pilot plant include a reference electrode for electrolysis voltage control, a potentiometric microelectrode for determining melt dryness, and automatic shutoff and telephone recording warning device in the event of crucible failure or heater shutdown. An ampere-hour integrator was used to determine the amount of UO_2 that should theoretically have been deposited during electrolysis according to Faraday's law. The electrolysis efficiency was then calculated using this figure compared to the weight of UO_2 deposited. Conventional recorders for temperature, voltage and current were also used. A description of other experimental apparatus such as liquid level indicators, continuous density recorders, and U(IV) photometers is given elsewhere. (22,23)

Reference Electrode Control System

The reference electrode voltage control system maintained the cathode-to-melt potential below the decomposition potential of the carrier salts. The components of the system are a reference electrode, a pH meter used as a millivoltmeter, a recorder-controller and a 500-amp 12-volt rectifier with an automatic voltage control system operating from the controller signal. The reference electrode is a Ag/AgCl half cell consisting of a quartz tube with a Pyrex membrane bottom. Its components are a 1 molal solution of AgCl in a 2.5 KCl-PbCl₂ melt surrounding a silver wire. A high impedance millivoltmeter is required to measure the reference electrode potential since only a few microamperes pass through the circuit because of the high resistance of the Pyrex membrane. The recorder-controller amplified the weak signal from the pH meter into a usable error signal for the automatic voltage control system on the rectifier.

The initial voltage of the reference electrode system is the sum of two half cell reactions.

The reference electrode

and at the cathode

The initial voltage is the sum of the two half cell reactions (approximately 400 mV) and decreases as the initial UO_2Cl_2 concentration of the melt is lowered.

In practice, an electrolysis was conducted for a few minutes to cover the surface of the cathode with UO_2 . The electrolysis was then stopped and the potential difference between the cathode and the reference electrode (about -400 mV) was read on the recording millivoltmeter. Then the electrolysis was resumed, and the potential as read on the meter was held at a predetermined usually positive value during electrolysis. The operating point was set below the decomposition voltage of the carrier salts (see Figure 12, page 38).

Dryness Test Apparatus

The potentiometric microelectrode system for determining the dryness of the melt operates on the same principle as the reference electrode control system. There are three electrodes used; a small anode, a reference electrode and a microelectrode for a cathode. The output voltage to the anode and cathode is controlled by maintaining a constant voltage across the reference electrode and the cathode. A plot of current versus time is recorded over about a 15-minute interval (see Figure 21, page 57). Since very little current is passed (less than 5 amperes) the concentration of the melt remains unchanged. Any change depends only on a change in the plating area of the microcathode. In wet melts dendritic deposits are made which tend to increase the area and hence give a positive slope to the current versus time curve. In dry melts the deposits are dense, flat and closely packed with very little change in surface area. A comparatively flat curve is obtained in this case. The curve may even have a negative slope for dry melts since there is an initial expansion of electrode deposition surface before the crystal formation becomes stable. A constant temperature must be maintained during the drying test to get meaningful results.

Crucible Breakage Alarm

An alarm system was installed on the heating system for the large crucible to provide early warning of crucible breakage at heater shutdown. The

device was activated by the shutdown of the motor generator for the induction heating coil. The motor generator was shut down by low pressure on the cooling water lines to the coil or the motor generator, by electrical failure, or by an automatic shut-off device activated by a leak in the molten salt crucible.

The shutoff after crucible breakage was accomplished by the molten salt short circuiting two wires placed in the annulus between the crucible and the secondary container. These platinum wires were in quartz tubes and they terminated near the bottom of the secondary container where molten salt would collect upon crucible breakage. Shutdowns due to water or electrical failures could be remedied before the melt in the crucible froze, minimizing crucible breakage and the resulting expensive and time consuming cleanup operations. If the crucible broke, immediate shutoff and notification prevented equipment damage and permitted prompt action to simplify the salt removal and cleanup work.

LEAD CHLORIDE-POTASSIUM CHLORIDE PILOT PLANT OPERATIONS

After it became clear from laboratory data⁽²⁴⁾ that lower operating temperatures could be achieved in a solvent of composition 2.5 moles KCl per mole PbCl_2 , pilot plant operations were started in this system. The primary incentives for the change were lower corrosion rates of graphite and metallic materials of construction and the possibility of producing larger deposits because of a lower rate of U(IV) buildup in the melt. The pilot plant operations in the 20 liter crucible are summarized in Table IX, page 55, and for the 80 liter crucible in Table X, page 63.

Dissolution

Dissolution of the UO_3 and U_3O_8 feed materials in the 2.5 KCl- PbCl_2 system was conducted with chlorine gas sparged through 6 mm quartz tubing. The temperature during dissolution was nominally 700 °C. Dissolution occurred readily when sufficient mixing of chlorine gas and the feed material was attained. Good mixing was obtained in small crucibles where the feed was easily fluidized but became poorer as vessel size increased.

Since the normal operating period was only 8 hr/day except for the last three runs (NPL 21-23), dissolutions were discontinuous and dissolution rate data were collected in only two cases.

The dissolution data for runs NPL-11 and NPL-12 in 20 liter crucibles is shown in Figure 20. The curves show a slow buildup of uranium in solution with the rate gradually decreasing as the feed material was dissolved. The amount of chlorine gas used is plotted on the same graphs to indicate the excess required to produce UO_2Cl_2 . In NPL-12, over 100% use of chlorine was observed during the first few hours. This was attributed to the solubility of U_3O_8 in the melt and to suspended oxide. U_3O_8 is soluble in the 2.5 KCl-PbCl₂ molten salt up to 5 wt%, increasing with UO_2Cl_2 concentration.⁽¹³⁾ The tests results indicated that dissolution was not a great problem in the smaller crucibles.

Some difficulty was experienced during dissolution of feed in the 80 liter crucibles. The chlorine sparge was insufficient to fluidize the feed, particularly after a dissolution has been discontinued overnight. However, dissolution usually went rapidly with pure feed. In the last few runs, feed with impurities including iron, sand, and metal turnings did not completely dissolve, and left inert impurities and U_3O_8 sludge in the bottom of the crucibles. This experience pointed out the need for a melt stirrer or circulator to promote fluidization of the feed for increased dissolution rates. A submerged gas-lift recirculator was developed after the conclusion of the studies in the 2.5 KCl-PbCl₂ system and was used in the LiCl-KCl system.

Drying

Two methods of drying the molten salt solution after completion of the dissolution step were tried in the last three runs of the series. One method involved further sparging with chlorine or hydrogen chloride gas. The other consisted of a pre-electrolysis step in which UO_2 was plated out on the anodes prior to the final electrolysis step.

Drying of molten salts with chlorine gas had been quite successful in the laboratory. The use of hydrogen chloride gas was even more effective than chlorine during uranium dioxide crystal growth studies by Chemical

FIGURE 20
Dissolution of U_3O_8 in $PbCl_2-2.5 KCl$

TABLE IX

PILOT PLANT ELECTROLYSIS IN THE LEAD CHLORIDE-POTASSIUM CHLORIDE SYSTEM

Twenty Liter Salt Bath

Salt System: 2.5 moles KCl/mole PbCl

Melt Weight: 100-130 lb total

Dissolution Temperature: 675-710 °C

Feed Material: UO₃ Powder, except as noted

DISSOLUTION						ELECTROLYSIS									
Run No.	Feed wt, lb	Moles Cl ₂ Mole U	Used per Dissolved	Avg Flow l/min	Time, hr	Average Cell Volts	REF. POTENTIAL Volts		Temp, °C	CONCENTRATION		Current Density amp/in ²		Time, hr	Current Eff., %
							min.	max.		Initial wt% U	Final wt% U	Initial	Final		
NPL-6	28		2.2	2.5	13.6	1.2	---	---	550-580	16.6	3.2	2.92	1.28	27.6	86.9
NPL-7*	40		1.7	2.4	12.6	1.3	---	---	525-565	22.5	12.2	1.29	0.77	46.5	81.4
NPL-8*	10		6.3	~ 2.	18.6	1.1	---	---	550-600	---	11.1	0.97	0.14	21.3	---
NPL-9*	20		2.3	2.	14	2.0	0.52	0.58	560-660	16.9	2.0	2.25**	---	23.0	46.
NPL-10*	5		10.4	2-3	12.4†	1.6	0.51	0.52	580-600	8.2	0.12	0.61**	0.12	17.4	---
NPL-12	25***		2.0	3.	10.	1.6	0.29	0.30	585-620	22.8	6.4	1.13**	0.14	23.0	87

ELECTRODES					PRODUCT									
Run No.	Cathode		Anode		Deposit		Density, g/cm ³		Impurities, ppm					Crystal Characteristics
	Material	Area, in. ²	Material	Area, in. ²	wt, lb	O/U Ratio	9u	0.06u	Pb	K	Cl	C		
NPL-6	Carbon	54.75	Carbon (2)	110	20.2	2.015	---	---	---	---	---	306	See Figures 22 and 24.	
NPL-7	Carbon (round)	72.	6-in. ID Annular Carbon (1)	635	23.5	2.030	---	---	1111	< 50	50	---	Long dendritic crystals on outside.	
NPL-8	Carbon (round)	72.	6-in. ID Annular Carbon with 12 1-in.- holes	635	78.	2.018	---	---	---	< 50	260	---	-----	
NPL-9	Carbon (round)	72.	Annular Carbon 6-in. diam	635	13.5	2.013	10.93	11.00	564	170	200	1250	Slightly dendritic.	
NPL-10	Hastelloy D	197.	Carbon (2)	110	---	---	---	---	---	---	---	---	Flat, plate-like, small. Some included lead.	
NPL-12	Hastelloy D	197.	Carbon (2)	110	14.3	< 2.01	10.74	10.88	1000	100	---	1500	Flat, plate-like, small, 12 ppm Fe, 100 ppm Ni.	

*Run began with salt from previous run.

**Chlorine sparge during electrolysis.

***U₃O₈ powder.

†Also dried with HCl at 3 liters/min for 40 min.

Research personnel.⁽²⁴⁾ Similar results were obtained during the last few pilot plant studies in the 2.5 KCl-PbCl₂ series. In the earlier runs the salt was not dried after dissolution since the magnitude of the effect of wet melts on crystal characteristics had not yet been determined.

The pre-electrolysis drying step was carried out by inserting three graphite electrodes in the melt, using the center electrode as an anode and the two outside electrodes as cathodes. A short electrolysis resulted in a deposit of powdery UO₂ on the cathodes and melt drying by the chlorine evolved at the anode. The center electrode or anode was then replaced by a product cathode and the electrical leads were reversed so that the uranium-bearing electrodes were the anodes during the product electrolysis. The poor grade UO₂ on the anodes was subsequently dissolved and dried with chlorine gas from the electrolysis reaction.

The effects of drying with a chlorine sparge, hydrogen chloride sparge and pre-electrolysis are illustrated in Figure 21. The drying curves for run NPL-21, in which all three methods were tried and in which a UO₂ product with an O/U ratio of 2.004 was produced, are shown. The drying curves are current versus time for a glass-sheathed platinum microelectrode operated at constant voltage. After an initial decrease in current while the cathode is being polarized, the slope of the curves indicate the approach to dryness. A positive slope indicates a wet melt while a flat or slightly negative slope indicates a dry melt. The wetter the melt the greater the magnitude of the positive slope indicated on the drying curve. (See page 51 for further description of dryness tests.)

The curves in Figure 21 show the gradual change from a wet to a dry melt. From the slopes of the curves it is apparent that a chlorine gas sparge at 700 °C was drying the melt. Further drying was obtained with hydrogen chloride gas at 600 °C. Pre-electrolysis at 600 °C continued the drying process as indicated by the nearly constant current versus time. Although the difference is not specifically shown here, drying at the electrolysis temperature is believed to be more effective than at the higher dissolution temperature.

FIGURE 21
Wetness Tests in PbCl₂-2.5 KCl With 30 wt% Uranium

The magnitude of the current on the drying curve is highly temperature dependent so that the current at 700 °C is higher than at 600 °C. The current is also affected by the microelectrode area, which varies because the apparatus is reassembled for each test. This accounts for the change in initial currents for drying curves run at the same temperature. The slope of the drying curve is the only useful factor in determining the melt dryness.

Electrolysis

The electrolytic deposition of UO_2 from a molten salt melt involved a number of variables including electrolysis voltage, current density, temperature, impurities, and melt "wetness" (the presence of interfering oxides and hydroxides chemically held in the melt). These variables were studied on the laboratory scale by Chemical Research personnel and provided direction to the pilot plant studies which primarily involved scale-up of the process and confirmation of laboratory data. Although there was good general agreement between the laboratory and pilot plant data, important effects were encountered in the latter which had not previously been extensively studied.

In the PbCl_2 system the electrodeposition of reactor grade UO_2 is highly dependent upon the electrolysis voltage. The electrolysis must be operated at a potential sufficiently below the decomposition potential of the carrier salts to prevent their deposition as an impurity in the UO_2 . Curves of reference potential versus current for the deposition of UO_2 and lead from KCl-PbCl_2 melts are shown in Figure 12, page 34. The deposition curve for lead from 2.5 KCl-PbCl_2 melts (in the absence of UO_2) is not shown in that figure, but it would be at a higher voltage than those presented. The operating range for electrolysis starts at the lowest potential at which UO_2 will deposit and ends just short of the potential for lead deposition. In practice the potential is set near the maximum to provide a high UO_2 deposition rate.

The initial plant runs in the 2.5 KCl-PbCl_2 system were made in a 20 liter fused silica crucible 9-in. diam and 30-in. high. Three types of cathodes were used in the tests. A cylindrical graphite cathode in an

annular anode and a rectangular graphite cathode with a rectangular graphite anode on each side were tried. A Hastelloy D cathode between two graphite anodes was also tested. Typical deposits on these cathodes are shown in Figure 22. The dryness of the melts could not be directly determined in the early runs because the method had not yet been developed. However, the product crystal characteristics and oxygen-to-uranium ratio of the pilot plant product were somewhat different than for laboratory runs made under completely dry conditions. A cross section of a typical deposit is shown in Figure 23. The O/U ratios did not exceed 2.04 (as compared to 2.02 specifications) in any of the 20 liter scale runs, indicating a relatively dry melt and atmosphere in spite of the use of only a single lid with air inleakage. The small surface-to-volume ratio of the 20 liter crucible promoted chlorine blanketing from the anode reaction, accounting for the comparatively low oxygen-to-uranium ratios obtained.

In the last three runs, NPL-9, 10 and 12 on the 20 liter scale, a reference electrode control system described on pages 50 and 51 controlled the electrolysis voltage. In one run (NPL-10) metallic lead was plated out during the electrolysis while operating at a high reference voltage. The next run (NPL-12) was operated at a voltage within the desired range and resulted in a product with good crystal structure without visible lead in the deposit. Hence, the usefulness of the reference electrode control system and the direct use of laboratory electrolysis potential data for pilot scale operations was established.

The pilot plant crucible size was increased to 80 liters which is full scale operation for reprocessing a single fuel element from the Plutonium Recycle Test Reactor. The results of these runs are presented in Table X. In the first run (NPL-13), 60 lb of UO_2 were deposited and in the second (NPL-14), 116 lb. The product in each case was the mace type UO_2 (shown in Figure 24) with oxygen-to-uranium ratios of 2.04 and 2.09, respectively. The melt atmosphere was a mixture of air and chlorine since the chlorine from the anode reaction was diluted by an air sweep to the off-gas system. The crystal shape and oxygen-to-uranium ratio indicated the melt was not completely dry. Uranium (IV) buildup in the melt was not detectable at the electrolysis temperature of 590 ± 20 °C.

Run NPL-6, 20 lb. Deposit on Graphite Cathode,
O/U = 2.015

Run NPL 13, 60.3 lb. Deposit on Hastelloy D Cathode,
O/U = 2.04

FIGURE 22
UO₂ Deposits from PbCl₂-2.5 KCl Salt System

Side Next to Electrode

Cross Section

Growing Surface

0.1"

FIGURE 23
Cross Section of UO_2 Deposit from PbCl_2 -2.5 KCl Salt Bath
Run NPL-6, O/U Ratio = 2.015

0.5"

FIGURE 24
Mace-Type Crystals from the PbCl_2 -2.5 KCl Salt Bath
Run NPL-14 O/U Ratio = 2.09

Salt System: 2.5 moles KCl/mole PbCl₂
Total Salt Weight: 482 to 658 lb
Feed Material: U₃O₈ powder
Cathode: Hastelloy D
Anode: Two flat carbon anodes with a
total submerged area of 110 in²

TABLE X
PILOT PLANT ELECTROLYSES IN THE LEAD CHLORIDE - POTASSIUM CHLORIDE SYSTEM
Eighty Liter Salt Bath

Run No.	DISSOLUTION				DRYING			ELECTROLYSIS								PRODUCT										Remarks	
	Feed Weight, lb		Moles Cl ₂ Used/ Mole U Dissolved	Time, hr	Average Flow, l/min	Time, hr	Maximum Cell Volts	Ref. Potential,		Temp, °C	Wt% U		Current Density, amp/in ²		Time, hr	Current Eff. %	Cathode, Area, in ²	Deposit Wt., lb	O/U Ratio	Density, g/cm ³		Impurities, ppm					
	Initially in Solution	U ₃ O ₈ Added						Avg	Max		Initial	Final	Initial	Final						9u	0.06u	Pb	Cl	K	C		
																											Gas
NPL-13	0.	100.3	2.95	29.0	Concurrent with dissolution		2.31	0.40	0.41	585-600	18.4	10.4	0.63	0.52	25.1	85.2	480	60.3	2.04	---	---	436	200	170	38 91 32	Mace-type, large crystals 270 ppm Fe, 30 ppm Ni	
NPL-14	37.8	100.0	1.45	14.5	Concurrent with dissolution		2.75	0.40	0.41	583-600	21.4	1.46	0.75	0.52	48.0	87.6	480	116.3	2.09	10.86	10.86	1000	---	580	348 162 128 742	Mace-type, large crystals 490 ppm Fe	
NPL-15	17.2	104.4	1.57	16.6	HCl	5.4	5.8	1.52	0.26	0.41	555-580	20.7	5.50	0.42	0.40	34.0	57.5	480	82.0	2.13	10.37	10.81	622	354	300	1256	Mace-type, fairly large crystals 400 ppm Fe
NPL-17	17.9	125.0	1.71	21.5	Concurrent with dissolution		2.17	0.32	0.34	600-620	13.7	6.72	0.89	0.23	30.3	72.5	480	87.0	2.026	10.71	10.86	925	13	180	279 205	Close packed dense outside, porous small grain on inside	
NPL-18	52.7	104.6	2.16	21.5	Concurrent with dissolution		2.80	0.35	0.37	590-600	22.7	9.14	0.92	0.29	51.0	79.4	444	86.0	2.028	10.72	10.86	592	300	400	---	Compact dense on outside, powdery deposit inside	
NPL-20	68.1	88.2	2.42	21.1	Pre-Electrolysis	3.8	2.00	0.44	0.46	580-650	23.8	18.0	1.20	0.22	65.0	79.3	162	40.0	2.011	---	---	---	---	---	---	---	Same as NPL-18
NPL-21*	85.0	95.6	5.44	54.5	HCl	6.	2.7	1.62	0.43	0.51	587-620	29.5	18.0	0.46	0.08	113.8	80.0	372	45.2	2.004	9.92	10.34	1600	200	210	---	Compact, dense, very good
NPL-22	133.0	96.0	3.09	40.0	HCl	3.	19.3	1.47	0.46	0.49	570-620	34.0	28.2	0.33	0.26	96.6	41.8	372	41.0	2.040	8.85	9.75	594	6000	3000	---	Powdery, fine, loosely agglomerated
NPL-23	186.5	81.2	9.95	86.3	Concurrent with dissolution		2.40	0.58	1.12	600-620	----	32.3	0.44	0.55	50.3	48.1	404	20.0 38.0	---	10.18	10.66	---	---	---	---	Dense, compact on inside Powdery, poor on outside	

*Frozen salt from NPL 20 crushed and remelted.

After it was established that UO_2 could be produced on a large scale in the 2.5 KCl-PbCl_2 system, further efforts were made to lower the oxygen-to-uranium ratio of the product. Laboratory-scale studies had indicated that a dry melt and a chlorine atmosphere were conditions necessary to produce low oxygen-to-uranium ratio UO_2 . Consequently, the drying methods discussed earlier were tested, and operation with a reduced air sweep over the melt was tried. The oxygen-to-uranium ratios were reduced to as low as 2.011 by these methods. However, the 8-hr/day operation during dissolution and drying did not lead to complete melt drying before electrolysis. Normally a small layer of powdery UO_2 was found near the electrode surface, with a dense layer of large UO_2 crystals comprising the remainder of the deposit. Since the electrolysis was a 24-hr/day operation, the melt was evidently dried by the chlorine from the anode reaction, accounting for the good outer layer.

A combination of changes was made simultaneously including (1) the development of a lid separating the crucible atmosphere into a lower chlorine zone and an upper zone containing the off-gas outlet and having atmospheric air inleakage, (2) 24-hour operation during dissolution and drying, and (3) the use of a method for determining melt dryness developed by Chemical Research personnel. These changes resulted in the electrodeposition of a dense, large crystal UO_2 product (Run NPL-21) having an oxygen-to-uranium ratio of 2.0036. This deposit left little doubt that the laboratory results could be scaled up to production size operation with proper equipment design.

Two further runs, NPL-22 and 23 were made in 2.5 KCl-PbCl_2 system which resulted in rather poor product. The crystal size was small and did not resemble any from the earlier runs. The poor results were attributed to impurities in the feed after similar results were observed in later electrolyses in the LiCl-KCl system. The feed was found to contain 1 wt% iron in addition to other impurities. It was later found that corrosion of the Hastelloy D cathode could also have contributed to the poor results.

Product Evaluation

The evaluation of the product for use as reactor grade UO_2 included determination of density, impurity content, oxygen-to-uranium ratio, and minimum

crystal size. Crystal size was generally adequate for high density vibratory compaction and, therefore, was only qualitatively evaluated for each run.

The available data for the product are shown in Tables IX (see page 55) and X (see page 63). The density, reported for -6 + 20 mesh particles, was measured with a mercury porosimeter with all open pores less than 9 μ diam considered as part of the UO_2 .

The major impurities in the product from the 2.5 KCl-PbCl₂ system were lead, chloride, and potassium with some iron and silicon. The lead and potassium were apparently occluded as salts. The soluble potassium chloride was rather easily removed with water but the lead chloride was difficult to remove even with the use of hot 0.5 M ethylenediaminetetraacetic acid (EDTA). Because of its greater weight and difficulty of removal, lead made up the bulk of impurities. In the pilot plant studies, the lowest concentration of lead in the product was 440 ppm. In previous laboratory studies, lead had been removed to as low as 50 ppm, indicating that with further development work the lead content of the pilot plant product could have been reduced.⁽²⁵⁾

The crushing and washing of the product from the pilot plant were investigated only as a sidelight in the transfer of the UO_2 to Ceramics Fuel Development personnel for evaluation. The UO_2 was crushed in a jaw mill to -6 mesh and then washed in a packed bed through which 0.1 M EDTA solution was circulated. The lead removal increased with increasing washing temperature and EDTA concentration of the wash solution. Since most of the early pilot plant product had an O/U ratio above the specification of 2.015, a hydrogen reduction to lower the oxygen was made by Ceramics Fuel Development personnel. In the process, lead, lead chloride, and potassium chloride impurities were volatilized, appreciably decreasing the lead impurity content as shown in Table XI.⁽²⁵⁾

TABLE XI

EFFECT OF HYDROGEN TREATMENT FOR 10 HOURS AT 1000 °C
ON SALT CONTENT OF ELECTRODEPOSITED UO_2

	<u>ppm K</u>	<u>ppm Pb</u>	<u>ppm Cl</u>	<u>O/U Ratio</u>
As electrodeposited-unwashed	1,400	12,100	1,100	2.013
After H ₂ treatment at 1000 °C	360	250	65	2.001

LITHIUM CHLORIDE-POTASSIUM CHLORIDE PILOT PLANT OPERATIONS

Lithium chloride-potassium chloride was the last of the systems investigated because of the highly hygroscopic nature of LiCl systems. LiCl, when exposed to the atmosphere at room temperature, absorbs water until an aqueous solution is formed. Laboratory studies by Chemical Research personnel showed, however, that even in this system the moisture which prevents deposition of stoichiometric UO_2 can be removed by sparging with hydrogen chloride or chlorine. The hygroscopic nature of this system increases strongly as the LiCl content is increased, and operations in pure LiCl would require much greater care in excluding the atmosphere than in equimolar LiCl-KCl. The advantages of the LiCl-KCl system over the PbCl_2 -KCl system are:

- The system can be operated at a lower temperature. Pilot plant dissolutions of U_3O_8 were conducted in the LiCl-KCl eutectic at 600 °C and electrolyses were carried out at as low a temperature as 500 °C, versus 700 °C and 600 °C, respectively, for the PbCl_2 -KCl system.
- The LiCl-KCl system is essentially nonvolatile under these conditions, with a boiling point of 1400 °C. The PbCl_2 -KCl system produced PbCl_2 vapors which clogged off-gas lines.
- LiCl and KCl have high decomposition potentials, so that they are not readily codeposited with the UO_2 and the occluded salt can readily be removed from the deposit by water washing. PbCl_2 was not readily soluble in water, and even extensive washing with complexing agents at elevated temperatures could not lower the lead content to acceptable limits. The low decomposition potential limited the range of operation of the process without depositing lead.
- The wide range of operating temperatures and solvent compositions in LiCl-KCl allows the carrying out of related processes such as precipitation, partition and codeposition which require higher operating temperatures or widely varying chloride activities.

A total of 510 lb of UO_2 was produced in 9 runs in the 80 liter pilot-plant quartz pot with 60 wt% KCl-40 wt% LiCl (46 mol% KCl-54 mol% LiCl). The results are reported in Table XII. Dissolution of U_3O_8 and drying of the melt were carried out at 600 °C in each case.

Dissolution and Drying in the 80 Liter Salt Bath

To ensure dryness of the melt the dual lid system described under the Equipment Section, page 47, was used throughout the LiCl-KCl pilot-plant

TABLE XII
PILOT PLANT ELECTROLYSES IN THE LITHIUM CHLORIDE-POTASSIUM CHLORIDE SYSTEM
Eighty Liter Salt Bath Containing Equimolar LiCl-KCl

Dissolution Temperature: 600 °C
Gas Lift Flow Rate: 4 l/min chlorine

Run No.	Residual U as U ₃ O ₈ , lb	U ₃ O ₈ Added, lb	ppm Fe in Feed	Total Melt Weight, lb	DISSOLUTION			Approximate Time, hr	DRYING				Uranium wt%		ELECTROLYSIS						
					Cl ₂ /U Mole Ratio	Chlorine Flow, l/m			Cl ₂	Time, hr	HCl	Time, hr			Cell Volts		Reference Potential Volts	Deposit Wt, lb	Temp, °C	Current Densitv, amp/in. ²	
						Gas Lift	Additional						Initial	Final	Avg	Final				Initial	Final
LK-24	None	110.1	High	388	9.6	3.2	3.0	150.	6**	4	---	---	20.0	10.9	---	2.13	0.74	39.3	515-520	0.90	0.84
LK-25*	52	57.8	High	387	10.5	4.3	1.8	71.	3**	51	---	---	20.3	11.3	---	2.00	0.32	36.0	360-560	0.33	0.08
LK-26	None	130.	170	345	10.2	3.5	3.0	144.	4***	23	2.0	59.	29.8	12.5	---	2.40	0.77	82.1	510-540	0.62	0.21
LK-27*	45	100.	---	360	6.7	4.0	3.0	---	6***	23	2.0	2.5	32.2	20.4	---	2.00	0.77	62.5	470-540	0.60	0.22
LK-28*	80	50.	530?	345	5.0	3.0	3.0	66.	3	19	2.0	14.0	28.2	(16.7)	1.97	2.42	0.76	48.0	500-535	0.54	0.46
LK-29*	58	None	270?	295	---	---	---	---	3	16	1.5	24.	(16.7)	5.3	1.30	1.38	0.48	50.0	535	0.46	0.20
LK-30	None	130.	60	345	5.6	4.4	3.0	48.	3	38	2.0	4.	29.4	14.5	2.30	2.40	0.88	73.0	535	0.95	0.60
LK-31*	54	80.	50	349	3.8	4.4	3.0	26.5	4	6	2.5	6.	26.3	17.9	1.25	1.38	0.51	44.5	530	0.64	0.23
LK-32*	90	41.	---	340	5.1	4.2	3.0	31.	4	38	1.0	10.	25.8	10.4	2.5	6.0	---	75.0	535	0.80	0.70

Run No.	ELECTROLYSIS			PRODUCT								Density, g/cm ³		Crystal Characteristics	Remarks
	Current Efficiency	Cathode		O/U Ratio	ppm Impurities										
		Area, in. ²	Material		Li	K	C	Ni	Fe						
LK-24	60	368	Carbon	0.0266	110	140	91	---	226	10.65	10.80	Walnut, small.	0.3 wt% Fe in melt.		
LK-25*	49	515	HastelloyD	2.0530	60	---	14	245	---	10.51	10.92	Powdery next to cathode, outside dendritic.	0.3 wt% Fe in melt. Melt became wet during a heater shutdown in the run.		
LK-26	73	374	Hastelloy D	2.0037	70	23	---	---	125	10.85	10.88	Very large, dense, flat large faced crystals.			
LK-27*	74	380	Hastelloy D	2.0050	30	---	---	---	115	10.11	10.62	Blistered, splotchy deposit bare oxidized cathode in spots. Fairly large, flat crystal.			
LK-28*	62	390	Duranickel†	2.0048(Metal) 2.0071(Carbon)	---	---	74	350	92	10.38	10.55	Small, dense and flat.	Initial melt contained 0.25 wt% Ni from corrosion of electrode in Run 27 and contained 0.54 wt% Ni at the end of electrolysis.		
LK-29*	70	263	Carbon	2.0107	---	---	---	---	185	10.85	10.90	Very thin, walnut, columnar.	Melt contained 0.52 wt% Ni from electrode corrosion during Run 28.		
LK-30	76	315	Carbon††	2.0023	---	---	116	---	120	10.79	10.84	Thin, columnar, almost walnut.	60 ppm Fe in salt.		
LK-31*	75	280	Carbon††	2.0006	---	---	253	4	140			Medium, small, columnar.	60 ppm Fe in salt.		
LK-32*	---	289	Carbon††	2.0025	---	---	285	---	170	10.78	10.87	Dense, columnar near cathode turning to soft and spongy on outside.	Constant current run. Reference potential exceeded salt decomposition voltage near end of run. 90 ppm Fe, 40 ppm Ni in salt.		

*Salt bath from previous run was used as the starting material for this run.
**During preelectrolysis.
***Anodes predried in oven.
†Protected by graphite at interface
††Hand polished pile graphite.

runs. The dryness testing apparatus was employed after each dissolution to determine whether the bath was ready for electrolysis. During trial operation in the first run (LK-24) in the LiCl-KCl salt bath a gas-lift recirculator was found qualitatively to fluidize the U_3O_8 powder much better than straight sparge tubes. In all LiCl-KCl pilot plant runs the dissolution of U_3O_8 was carried out with a gas-lift recirculator using chlorine, with additional chlorine introduced into the melt with straight sparge tubes.

In the initial run (LK-24) the bath was dried with chlorine for several hours before 110 lb of U_3O_8 were introduced in 4 batches over a 27 hr period. Chlorine was sparged intermittently into the bath with the gas-lift system until the dryness test showed a small positive slope (not quite dry). Then graphite electrodes were inserted and the bath was pre-electrolyzed for 5 hr. The dryness test then indicated no increase in current with time, so that the salt was ready to electrolyze. The O/U ratio of the product was 2.027, indicating that the bath was not completely dry. The crystal structure was poor, and this was tentatively attributed to the iron in the feed.

A second run (LK-25) was made with the same melt as above. U_3O_8 was added to the melt to replace the UO_2 deposited. The bath was then sparged continuously with chlorine for 80 hr. The dryness test indicated a very dry melt. A pre-electrolysis with graphite electrodes was then carried out for 6 hr at 1.6 V and 210 amp at 520 °C. The graphite electrodes introduced some water into the melt as shown by foaming and spattering of the bath during introduction of the electrodes. However, a subsequent dryness test indicated the melt was nearly dry. During the subsequent electrolysis with a Hastelloy D cathode, power was accidentally cut off allowing the bath to cool. Before power resumption a crust had formed on top and the electrodes froze, interrupting the electrolysis for at least one hour. Since the chlorine blanket produced by the electrolysis was not present during this period the external atmosphere penetrated to the salt bath and moisture was picked up by the bath. The electrolysis was continued, but the damage had already been done and the average O/U ratio of the deposit was 2.053.

Because of the iron introduced by the impure feed, the salt from runs LK-24 and 25 was discarded and a fresh salt bath was used in Run LK-26. About

130 lb of U_3O_8 , charged in several small batches, was dissolved by sparging with chlorine gas continuously for 120 hr followed by drying with HCl gas for 16 hr. The dryness test showed a dry melt and the electrolysis was carried out with electrodes which had been predried at 100 °C for 24 hr. The oxygen-to-uranium ratio of the product was 2.0037 and the crystal structure was ideal, indicating that adequate dissolution of the U_3O_8 and drying had been attained. A continuous sparge of chlorine or hydrogen chloride is necessary to prevent even the molten salt from reabsorbing moisture from the atmosphere. All subsequent runs were carried out in a similar manner to run LK-26. The O/U ratio varied from 2.006 to 2.0107 in these runs, averaging well below the desired maximum ratio of 2.01.

In an effort to reduce the excess of chlorine needed and to seek a minimum time cycle for dissolution and drying, a 24-hr dissolution test was carried out in Run LK-31 at 600 °C. U_3O_8 feed was added in two 30-lb increments at zero and 8 hr and a 20-lb increment at 16 hr. The U_3O_8 slurry was circulated through the gas lift by chlorine and additional chlorine was introduced through a sparge tube. In Figure 25 the results of this test are compared with the dissolution in Run LK-30. Drying was carried out with two carbon rods in place using hydrogen chloride and chlorine at 530 °C.

The rate of dissolution was, of course, most rapid after each incremental U_3O_8 addition, with little U_3O_8 left to dissolve in the last 4 hr of each 8-hr period. From Figure 25 it appears that with continuous addition or with properly timed increments the dissolution could be completed in less than 12 hr. Drying was complete in less than 4 hr, but examination of the dryness test curve indicated that 2 hr would be sufficient, making a 12- to 14-hr dissolution-drying time cycle probable.

The effectiveness of dissolution and drying can be determined adequately for control purposes by the dryness test conducted before electrolysis. Crystal structure although influenced profoundly by the O/U ratio is also influenced by electrolysis conditions, electrode composition, and impurities in the bath. Final proof of the adequacy of dissolution, drying, and atmosphere control is given only by the oxygen-to-uranium ratio of the product.

FIGURE 25
Dissolution of U_3O_8 in Equimolar LiCl-KCl in the 80 Liter Salt Bath

Electrolysis and Product Evaluation from 80 Liter Pilot Plant Runs

Electrolyses in the KCl-LiCl system were carried out at 530 °C, with deviations as noted in Table XII. The atmosphere was chlorine produced at the anode and contained by the dual lid system developed in the PbCl₂-KCl runs. The influence of the imposed electrolytic conditions on the UO₂ product was masked in Runs LK-24 and LK-25 by the wetness of the melt and in subsequent runs by impurities in the system introduced by the feed and by corrosion of electrodes. The crystal structures produced in these runs are shown in Figures 26 and 27.

In Run LK-24 the electrolysis was carried out at an average reference potential of 0.74 volts and a current density of 0.85 to 0.90 amp/in.² with electrodes made of reactor grade graphite. The product had a high O/U ratio (2.027) but a relatively high density with small crystals. A lower reference potential of 0.32 volts and a Hastelloy D[®] cathode were used for Run LK-25 but the deposit was dendritic because of moisture introduced by poor atmosphere control during a heater shutdown.

Examination of the portion of the deposit next to the electrode, which was deposited before the operating difficulties occurred, revealed a powdery mass similar to that in LK-24. Analysis of the feed for these runs showed 0.35 wt% iron, and the deposits for runs LK-24 and 25 contained 230 and 380 ppm iron, respectively. The poor crystal structure could then be due to either the wetness of the melt or the iron impurities. In the subsequent runs feeds containing about 100 ppm iron were used, and all melts were sufficiently dry so that the drying and dissolution did not affect the product quality.

The electrolysis for Run LK-26 was carried out with a Hastelloy D cathode at a reference potential of 0.77 volts and a maximum current density of 0.62 amp/in. The average production rate during the 48-hour electrolysis was 1.7 lb/hr at a current efficiency of 73%. Even though the Hastelloy D was protected cathodically it corroded somewhat beneath the deposit, producing a thin corrosion layer. The deposit was composed of large, dense crystals with flat growing faces and had an O/U ratio of 2.0037. Run LK-27 was made under the same conditions. The same Hastelloy D cathode was reused; a

Run LK-24

Run LK-25

Run LK-26

Run LK-28

0.1"

O/U = 2.027
Wet Melt
Graphite Cathode

O/U = 2.053
Wet Melt

O/U = 2.004

O/U = 2.005
Severe Corrosion

FIGURE 26
UO₂ Deposits on Hastelloy D Cathodes from 80 Liter LiCl-KCl Salt Baths

FIGURE 27
 UO_2 Deposits on Graphite Cathodes from 80 Liter LiCl-KCl Salt Baths

similar deposit was obtained except that the thickness varied considerably along the surface of the cathode with splotches of thick deposit surrounded by thinner layers of UO_2 . In some places the cathode was exposed completely and experienced considerable corrosion at these spots. It was concluded that the corrosion products had accumulated sufficiently on the cathode to reduce the current flowing in certain areas. The corrosion of Hastelloy D is more severe in the LiCl-KCl system than in the $\text{PbCl}_2\text{-KCl}$ system and the electrodes are unsuitable for reuse. After Run LK-27 the melt contained 0.25 wt% nickel from electrode corrosion. Run LK-28 was carried out with a Duranickel[®] cathode protected at the interface with a carbon slab which extended below the surface of the melt. The Duranickel was severely corroded particularly at the region directly below the graphite protector. This may have been due to an electrochemical interaction between the graphite and the Duranickel. At the beginning of this run the melt contained 0.25 wt% nickel and at the end it contained 0.54 wt% nickel, all from corrosion of the electrodes, but the deposit contained only 350 ppm nickel, which is a decontamination factor of about 50 from the initial uranium. The deposit that was produced consisted of relatively small crystals and Figure 26 shows that corrosion of the Duranickel certainly degraded the crystal structure of the deposit.

Run LK-29 was then made with graphite cathodes at a reduced reference potential of 0.48, and beginning with the 16.7 wt% U terminal concentration of the previous run, the uranium concentration was lowered to 5.3 wt%. A dense product was obtained but a walnut-type, small-crystal deposit resulted. Although a number of variables were changed, the poor crystal structure was tentatively attributed to the nickel present in the melt.

Because of the impurities, the melt was discarded and a fresh bath was electrolyzed in Runs LK-30 and 31. Carbon anodes were used in both runs, with the only major variable being the reference potential, which was 0.88 volts in Run LK-30 and 0.51 volts in Run LK-31. The reduction in reference potential, accompanied by a reduced current density, did not affect the overall current efficiency, which was 75% in both runs. However, a much

[®] International Nickel Company

smoother growing surface and a higher density at 9 μ pore size was obtained at the lower reference potential (10.618 versus 10.825 g/cm³). The crystals were also somewhat larger in the low potential run. These runs also excluded reference potential as a prime factor in producing walnut-type deposits.

Run LK-32 was made at constant current. The crystals produced initially were unusually large and well defined (Figure 27). Toward the end of the run the reference potential exceeded the deposition potential of lithium and potassium as is shown in Figure 28. This resulted in chaotically oriented small crystals with the growing surface containing many craters. The precise cause of these craters is not known, but the use of a very high reference potential or operation at constant total cell voltage can result in poor UO₂ crystals because of deposition of alkali metals. In addition, lithium reacts with graphite with catastrophic corrosion. This did not occur here, apparently because the graphite was protected by the UO₂ deposit covering it.

Effect of Impurities on Deposit Crystal Structure

Because of the poor crystal structure of the deposits produced with metallic cathodes and the apparently detrimental effect of impurities in the feed, a series of runs was made in a two liter crucible with controlled addition of various metallic impurities to the bath.⁽²⁶⁾ The results are reported in Table XIII. The major differences in operating conditions between these tests and the pilot plant runs were the use of an HCl sparge and graphite electrodes during the electrolysis.

Nickel, a major component of the Hastelloy D cathode, had no apparent effect on the deposit and a melt-to-deposit decontamination factor (DF) of 3000 to 10,000 was obtained for nickel from uranium. Aluminum only had a DF of 10 to 20 and had a strongly detrimental effect on the UO₂ crystals. Iron had a DF of 1000 and a weaker effect than aluminum. Manganese and the fission products zirconium, molybdenum, niobium and samarium had no apparent effect. Chromium tended to electropolish the deposit and had a DF of 1000 to 3000. The fission product molybdenum volatilized from the salt bath, apparently as the chloride.

These results indicate that impurities in the bath itself do not have as strong an effect on crystal structure as dynamic corrosion of the cathode. In

FIGURE 28
Reference Potential Variation in Constant Current Electrolysis

TABLE XIII

EFFECT OF IMPURITIES ON ELECTROLYSES IN LITHIUM CHLORIDE - POTASSIUM CHLORIDE

Salt Weight = 2200 g equimolar LiCl-KCl
 Feed Material = $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ or UO_3
 Sparged HCl for 24 hr after impurity addition
 Initial U = 20 to 25 wt%
 Final U = 10 to 15 wt%
 Materials = Fused silica crucible, graphite electrodes
 Cell Voltage = 2.5 to 3.0 V
 Reference Potential referred to 1 m AgCl in $\text{PbCl}_2 \cdot 2.5 \text{ KCl}$ = +0.6 V
 Electrolysis Time = 24 hr
 Bath Temperature = 530 °C
 HCl sparge during electrolysis

Run No.	Added Chemical	Wt% Metal into Salt Bath	ppm in Deposit	DF	Current Efficiency	O/U Ratio	Density,** g/cm ³	Remarks, Deposit Characteristics
2	Fe°	1.0	120	1,000	60	2.0067	9.80	Porous structure, melt was opaque due to FeCl_3 .
3	None	---	---	---	94	2.0029	10.59	Control.
4	Fe°	1.0	100	1,000	61	2.0022	10.46	Highly electropolished, porous, small crystals. Fe caused a reduced current efficiency.
6	Ni°	0.79	4	11,000	90	2.0009	10.91	No apparent effect.
7*	Al°	0.1	200 11 Ni	18 3,600 Ni	100	2.0015	10.83	Very poor, porous deposit, small crystals.
8	Sm_2O_3	0.42	---	---	94	2.0014	10.92	No apparent effect.
9*	Al°	0.25	1200	9	81	2.0005	10.68	Porous structure, precipitate.
10	AlCl_3	0.25	---	---	91	---	9.54	Porous structure, small crystals, precipitate - melt was opaque after Cl_2 flow was interrupted for about 2 hours.
11	Zr° Nb°	0.40 0.40	---	---	---	2.0021	10.80	Large columnar crystals, deposit surface porous.
12	Nb°	0.80	---	---	76	2.0011	10.73	No apparent effect - melt very deep red.
13	Zr°	0.40	---	---	100	2.0016	10.81	No apparent effect.
14	CrO_3	0.40	7	3,100	108	2.0004	10.84	Highly electropolished surface, only 10% of Cr found in salt, melt was opaque after HCl sparge started.
15*	Mo°	0.74	20 Cr	1,100 Cr	79	2.0019	10.32	Molybdenum volatilized as chloride, melt was brown and opaque at completion of run.
16	MnO_2	0.58	---	---	104	---	---	No apparent effect; solution was opaque when the MnO_2 was first added. Changed to clear normal color after sparging with HCl overnight.

*Salt from previous run with added uranium.

**Density determined with a mercury porosimeter includes closed pores and pores less than 9μ diameter.

other laboratory studies⁽²⁷⁾ impurities were found to increase the chloride content of the deposit, apparently through the formation of oxychlorides, such as MoOCl and FeOCl , which were included in the deposited UO_2 and which could not be leached from the deposit with water.

Hot Cell Prototype Operations

The LiCl-KCl system was selected for the Salt Cycle demonstration,⁽²⁸⁾ and the remotely operable equipment shown in Figure 29 was tested in the pilot plant. A double lid made of Hastelloy B[®] with stainless steel fittings was used. Lavite gaskets separated the chlorine-rich salt chamber from the exhaust chamber into which air leaked through the upper part of the lid. The effectiveness of this system in maintaining a dry atmosphere is discussed in a separate report.⁽²⁹⁾ The salt in the 20 liter fused-quartz crucible was kept molten by induction heating of the Hastelloy B susceptor by a 3 kc coil. All connectors were remotely operable. The susceptor was insulated with a 1/4-in.-thick layer of potassium titanate held in place by asbestos cloth and surrounded by a 1/2-in.-thick free-standing Magnefrax[®] insulating shield. The induction coil was insulated with glass sleeving set in Doryl[®], and the air gap between the coil and susceptor was about two inches. Nearly 6 kW were required to keep the crucible at operating temperature, with a division of 1.3 kW generated in the coil and removed by the cooling water, 2.1 kW transferred from the susceptor to the coil through the insulation and removed by the cooling water, and 2.4 kW transferred from the susceptor and the salt bath to the atmosphere.

Aside from remote mechanical operability tests and the demonstration of an ability to process 30-lb batches of U_3O_8 , the major purposes of the operations in the prototype equipment were to develop a suitable cathode material and to produce a standard product to be used in development of remotely operable crushing and sieving equipment. A summary of the prototype pilot plant runs is presented in Table XIV.

Electrolysis operations were first conducted in 1:1 LiCl-KCl in which codeposition of UO_2 and PuO_2 was most likely to be carried out, and then in 2.5:1 LiCl-KCl , in which precipitation of PuO_2 might be conducted as part of

[®] Union Carbide Company

[®] The Carborundum Company

[®] Westinghouse Electric Co.

TABLE XIV
HOT CELL PROTOTYPE ELECTROLYSES

Salt System - 60 lb LiCl-KCl mixture.
Scale: 20 liter fused silica crucible, 9 in. diam.
2 Pile Graphite Anodes, 1/4 in. x 3/4 in. x 21-1/4 in. below lid.
Cathode - 1.51 in. diam x 36 in. length. About 18 in. submerged in salt.
Micro-electrode trace to determine moisture in salt before electrolysis.

Run No.	DISSOLUTION					DRYING					ELECTROLYSIS						PRODUCT										Remarks
	U ₃ O ₈ Feed Wt, lb	Temp, °C	Rate, l/min	Time, hr	Cl ₂ /U Mole Ratio	Gas Rate, l/min		Temp, °C	wt% Uranium in Salt			Cell Voltage		Temp, °C	Current Eff. %	Cathode Material	Time, Hr	Average Current Density, amp/in. ²	Deposit Wt, lb	Density, g/cm ³		O/U Ratio	Carbon, ppm				
						Cl ₂	Time, hr		HCl	Time, hr	Before Dissolution	Before Electrolysis	After Electrolysis							Avg.	Max.			9u	.06u		
1 LiCl:1 KCl Salt Bath																											
HS-1	30	600	~ 2.0	72.0	7.9	1.2	23.0	1.0	23.0	535	none	26.4	4.04	1.20	1.40	540	70.9	Pile Graphite	28.5	0.85	24.6	10.95	10.97	2.0129	115	Sheared product from cathode with hydraulic jack.	
HS-2*	30	600	2.4 ~ 48.0		6.3	1.2	20.0	1.2	23.5	600	4.0	28.9	9.38	1.53	2.19	535	70.0**	Pile Graphite	25.0	0.94	24.6	10.90	10.92	2.0023	25	Cl ₂ sparge time is approximate as a cylinder ran empty during the night.	
HS-3*	55	600	2.4	53.5	3.9	1.2		2.0	20.0	550 to 600	9.4	39.0	24.9	1.85	2.20	535	58.1**	Pile Graphite	---	1.58	32.4	10.86	10.94	2.0018	20	Cathode was grounded during part of electrolysis. This caused a flat spot on the deposit.	
HS-4*	none added	600	1.2	3.5	---	1.2		2.1	48.0	535	24.9	24.9	1.4	2.0	2.27	535	73.8	Pile Graphite	19.9	1.06	21.5	10.88	10.92	2.0040	60	Deposit was quite porous and full of salt. About 1/8 in. of sandy deposit on outside; looked good under this.	
2.5 LiCl:1 KCl Salt Bath																											
HS-5	30	600	3.7	55.0	11.2	0.64		1.0	120.0	535	none	26.3	7.8	1.43	1.75	562	69.1**	Pile Graphite	24.1	1.09	20.0	10.87	10.91	2.0081	15	Had to increase temperature to electrolyze with this salt.	
HS-6*	30	620	3.0	57.0	9.4	1.8		1.0	5.0	575	7.8	25.7	16.3	1.35	1.51	565	67.4	Pyrolytic Graphite Coating	24.6	1.18	21.5	10.84	10.89	2.0124	23	Cl ₂ sparge time is approximate since cylinder ran empty over night. Salt had formed at 1.5 in thick bridge between anodes, cathode, and pot wall.	
HS-7*	20	620	2.0	26.0	4.6	1.0		1.0	20.0	570	10.1	29.3	10.1	1.52	1.86	570	75.6	Pyrolytic Graphite Coating	21.0	1.57	24.3	10.67	10.88	2.0068	25	Deposit broke away from cathode with no visual loss of carbon.	
HS-8*	25	700	3.0	24.0	4.8	---	---	1.0	26.0	565	14.6	31.3	14.9	1.40	1.48	565	62.5	Pyrolytic Graphite Coating	24.6	1.32	19.2	10.83	10.91	2.0015	22		
HS-9	31	600	2.3	27.0	3.3	1.0		1.0	22.5	600	none	26.0	13.0	0.90	1.20	555	52.2	Pyrolytic Graphite Coating	35.5	1.18	17.4	10.86	10.89	2.0308	7	Dissolution study using 9 in. long gas lift with Cl ₂ .	

*U₃O₈ added to salt from previous run
**HCl sparge during electrolysis

Twenty Liter Salt Bath

Electrolysis Lid

FIGURE 29
Hot Cell Prototype Equipment

the integrated operations. Essentially no difference in U_3O_8 dissolution or UO_2 electrodeposition was found between the two salt bath compositions, except that an increased operating temperature was required to keep KCl from freezing out of the 2.5:1 salt bath.

The dissolutions in Figure 30 show that with single 8 mm quartz sparge tubes an increase in dissolving rate was obtained by increasing the temperature from 600 °C to 700 °C and increasing the chlorine rate from 2 to 3 liters/min. Comparison of the suspended, undissolved U_3O_8 in Figure 31 with Figure 30 shows that a submerged annular gas lift is quite effective in fluidizing U_3O_8 . The solids were not uniformly distributed throughout the bath so that the weight percent solids at the sample point about 6 inches above the bottom of the crucible can only be interpreted qualitatively. In spite of the better fluidization, the dissolution rate was slower in Figure 31 because the dissolution of U_3O_8 is speeded up by the presence of dissolved UO_2Cl_2 . Thus, a characteristically increasing rate of dissolution with time is obtained until the amount of undissolved U_3O_8 decreases sufficiently to again reduce the rate.

The higher than stoichiometric concentrations of uranium in the salt in the early stages of dissolution are not due to suspended solids but to the solubility of U_3O_8 and the formation of lower chlorides such as UO_2Cl_2 . Such behavior has also been noted in $PbCl_2$ -KCl pilot plant operation. The solubility of U_3O_8 has been found to be greater in systems with high concentrations of dissolved UO_2Cl_2 .⁽³⁰⁾ This may be the explanation for the increased rates of dissolution found in nearly all pilot plant runs in which dissolved UO_2Cl_2 remains from previous runs made in the same bath.

The dryness testing apparatus was used in all runs to determine whether the bath was ready for electrolysis. Since this apparatus was too cumbersome to be used in hot cell operations, the dissolution and drying times developed in the prototype runs were used as guides to hot cell operation.

Although the reference potential system was built for hot cell runs, it was to be installed in the same lid port from which the samples were to be taken because of space limitations. Since removal of the reference electrode each time a sample was taken proved to be unworkable, the total cell voltage was used to control the electrolysis in the prototype runs. Figure 32 shows the relationship between the reference potential and the total cell voltage.

FIGURE 30
Dissolution of U_3O_8 in 2.5 LiCl-1 KCl

FIGURE 31
Dissolution of U_3O_8 in 2.5 LiCl-1 KCl with a Gas Lift

FIGURE 32
 Voltage-Current Relationships in the Hot Cell Prototype Equipment

With no current flowing, the reference potential is nearly independent of the wt% uranium in the bath, while the total cell voltage is higher for 9.4 wt% U than for 25.0 wt% U. The difference in total cell voltages is apparently due to a difference in the reactions at the anodes at the two concentrations. Both the reference potential and the cell voltage increase linearly as the current is increased indicating that the resistance of the cell is nearly constant, but the 25 wt% U system has a lower resistance than the 10 wt% U system. Although the possible importance of the contact resistance of the leads to the cathode cannot be ruled out, the major difference between the two systems is the existence of a polarized layer around the cathode at the lower concentration. The 25 wt% U system had a 1/3 larger deposit of UO_2 on the cathode during the test, which indicates that the UO_2 deposit resistance is not the most important part of the resistance of the cell. The thicker UO_2 deposit could actually lower the resistance of the cell in this case by increasing the total surface area of the cathode and reducing the current density at the surface. In practice, within the region of constant cell resistance, the cell voltage and reference potential as a function of concentration can be estimated at zero current for a given apparatus; and a constant difference due to cell resistance can be subtracted from the cell voltage to estimate the reference potential at any operating current.

The crystal characteristics of the product of the hot cell prototype electrolyses, shown in Figure 33, were remarkably constant although the uranium concentration varied from 39 wt% to 1.4 wt% in the series. Only at the lowest concentration was a porous, sandy structure noted. A typical deposit on a 1.5-in. diam graphite cathode is shown in Figure 34. Deposit weights varied from 17 to 32 lb. The reproducibility of the runs is attributed to (1) the long drying times which removed the last traces of moisture and undissolved solids, (2) the lack of impurities in the bath because of pure feed and the use of graphite electrodes, and (3) the narrow range of current densities that resulted in the same small degree of redissolution of the UO_2 while it was depositing.

The product of the first five electrolyses was of little use for crushing studies since it could not be separated from the pile-graphite electrodes.

Growing Surface

Cross Section

0.10"

FIGURE 33
Crystal Characteristics of Hot Cell Prototype Electrolysis Product,
Run HS-5 O/U Ratio = 2.008

1.5 in. Diam. Pyrolytic Graphite Cathode,
Deposit Weight 17.4 lb.

Run HS-9

FIGURE 34
Typical Deposit from the Hot Cell Prototype Electrolysis

The introduction of pyrolytic graphite cathodes, discussed under cathode evaluation (page 103), allowed the material from later runs to be treated as a standard product for stripping, crushing and washing studies. The relatively low carbon contents in the UO_2 produced on pile graphite are values in the bulk of the deposit and do not include the attached layer of carbon at the electrode surface.

Product Purification

A comparison of the composite products from the LiCl-KCl salt baths is shown in Table XV. After crushing, the fines contained higher percentages of oxygen and carbon than the bulk of the material that was in -4 + 10 mesh range. This is reasonable because the high O/U material was deposited first as small crystals next to the electrode where the carbon content was highest. The chloride and lithium contents were only a weak function of particle size.

The product from Run HS-8 was removed from the electrode as large chunks, rinsed with water to remove surface chloride, and was crushed and sieved. The results of a washing study on this material are presented in Table XVI. Each screen fraction of the oxide was washed with tap water for varying time periods in shallow beds on sieve plates. Although the tap water contained 2.75 ppm chlorine, control experiments with distilled water showed no effect of this chlorine on the results. Both the lithium and chloride analyses, although somewhat scattered, showed that washing times up to 480 hr on particle sizes ranging from 0.09-in. to 0.75-in. diam had no effect on the impurity level. The salt is apparently trapped within the UO_2 and cannot be leached out with water. Since the deposit was formed in a 2.5 LiCl-1 KCl salt bath, which has a mole ratio of lithium-to-chloride of 0.71, one may speculate that either the chloride analysis is consistently high, that the lithium analysis is consistently low, or that chlorides of impurities such as FeOCl are preferentially present in the deposit. Spot checks of the Li/K ratio indicate that KCl may enrich in the deposit over LiCl enough to account for the excess chloride, so that preferential adsorption of KCl on the deposit, or deposition and redissolution of small amounts of potassium metal at the cathode might explain the

TABLE XV
CHEMICAL ANALYSIS OF COMPOSITE PRODUCT
FROM LiCl-KCl PILOT PLANT OPERATIONS

Composite of HS-1, 2, 3, 4, 9
(Pile Graphite Cathode)

<u>Tyler Mesh Size</u>	<u>O/U Ratio</u>	<u>ppm C</u>	<u>ppm Cl</u>	<u>ppm Li</u>
-4 +10	2.007	152	28	10
-10 +35	2.024	---	---	20
-35 +65	2.028	---	---	32
-65	2.043	517	---	34

Composite of HS-5, 6, 7, 8
(Pyrolytic Graphite Cathode)

-4 +10	2.009	23	---	18
-10 +35	2.015	---	---	18
-35 +65	2.027	---	---	22
-65	2.031	31	158	18

Composite of LK-26, 27, 28, 29, 30, 31, 32
(Pile Graphite and Hastelloy D Cathodes)

-4 +10	2.007	528 115	---	14
-10 +35	2.005	---	53	33
-35 +65	2.004	---	183	30
-65	2.021	760	---	41

TABLE XVI
CHLORIDE ANALYSES IN AQUEOUS WASHING STUDIES

Feed Material: Screen Fractions of Run HS-8

Treatment: Washed with tap water containing
2.75 ppm Cl continuously by flow
through a shallow packed bed.

<u>-8 +10 Mesh Particles</u>				<u>-4 +6 Mesh Particles</u>			
<u>Washing</u> <u>Time, hr</u>	<u>Average</u> <u>ppm Cl</u>	<u>ppm Li</u>	<u>Mole Ratio</u> <u>Li/Cl</u>	<u>Washing</u> <u>Time, hr</u>	<u>Average</u> <u>ppm Cl</u>	<u>ppm Li</u>	<u>Mole Ratio</u> <u>Li/Cl</u>
Feed	323	18**					
2.5	274	11	0.20	5.0	331	15***	0.23
5.0	246			8.0	213	11	0.26
8.0	230	13	0.29	21.0	221	14	0.32
21.0	221	14	0.32	35.0	214	17	0.40
480.0	268	14	0.26	50.0	236	14	0.21
				480.0	280*		
				480.0	260*		

<u>-3/8 in. +3 Mesh Particles</u>		<u>-3/4 in. +1/2 in. Mesh Particles</u>	
<u>Washing</u> <u>Time, hr</u>	<u>Average</u> <u>ppm Cl</u>	<u>Washing</u> <u>Time, hr</u>	<u>Average</u> <u>ppm Cl</u>
Feed	218		
21.0	292	76.0	362
35.0	320	171.0	269
76.0	155	312.0	422
171.0	278	480.0	231
480.0	274		
480.0	250*		

Overall Average 270 ppm Cl

*Reanalysis approximately one year later.

**K = 80 ppm, Li/K mole ratio = 1.25 in deposit.

***K = 90 ppm, Li/K mole ratio = 0.93 in deposit.

results. Because particle size had no apparent effect on the washing efficiency in this study, the large 1/2 to 3/4 in. diam chunks of oxide were washed for only a few hours in the Salt Cycle demonstration⁽⁷⁾. This proved to be an advantage in the operating of the equipment, since fines entrainment in the wash liquor is minimized and after the drying operation the large pieces of oxide can be poured readily without dust formation.

Hydrogen reduction of high O/U ratio UO_2 was readily accomplished in the oxidizer furnace with argon - 8 vol% hydrogen at 600 to 700 °C for 24 hr. The results in Table XI (page 65) for lead chloride removal at 1000 °C indicate that high temperature hydrogen reduction might also be useful in removing chloride, although it is doubtful whether the chloride occluded within the UO_2 would migrate even at 1000 °C.

ELECTRODE EVALUATION

The choice of electrodes in the Salt Cycle system is limited by the corrosive environment and by the need to separate the UO_2 deposit from the electrode. At first, pile-graphite cathodes were used both as cathodes and anodes.

Graphite was replaced by Hastelloy D as the cathode material in the PbCl_2 -KCl system because of carbon contamination of the product by mechanical interlocking, but excessive corrosion in the LiCl-KCl system caused a return to graphite. The eventual development of pyrolytic-graphite-coated electrodes solved the cathode material problem for the Salt Cycle demonstration.

Anodes

At the 700 °C temperatures of the NaCl-KCl system the corrosion of the graphite anodes by chlorine resulted in U(IV) production that severely limited the recovery of UO_2 from the bath. At the 550 °C temperature of the LiCl-KCl system this reaction was negligible in its effect on the UO_2 deposition. However, traces of U(IV) present greatly influence plutonium behavior^(6,23) during codeposition.

In some runs the anodes were coated with MgO to prevent air oxidation in the vapor space. Although this retarded oxidation, the salt crept up under the MgO and sloughed it off near the interface.

Silicon carbide anodes and cathodes invariably developed a very high resistance immediately after being inserted in the bath. This may be related to the formation of an SiO_2 coating.

Metallic Cathodes

Platinum made an excellent material for cathodes except that it suffered accelerated interfacial corrosion. The 20-mil-thick platinum sheath on a nickel cathode used in an electrolysis in the NaCl-KCl system at 700°C corroded through at the salt-vapor interface in less than 30 min. Examination of the knife-like cut showed that chlorine gas had apparently reacted with the platinum and redeposited it in the vapor space next to the corroded area. Similar but not so severe corrosion occurred in the LiCl-KCl system. The platinum cathodes were never attacked below the salt level in either system.

To overcome this difficulty, tests were made with a $3/4$ -in.-diam, 12-in.-long platinum-sheathed electrode protected with quartz at the melt interface, shown in Figure 35. It was necessary to flare the quartz sheath to keep

FIGURE 35
Platinum Electrode Sheathed with Quartz, Run CT-4

the UO_2 from growing over it. Even then the UO_2 stuck to the quartz, so a pyrolytic graphite parting coat was put on the bottom of the quartz flare. The electrode still proved unsuitable because the salt crept up 2 or 3 in. by capillary action between the close fitting quartz sheath and the platinum.

Of the other metallic cathodes only Hastelloy D and Duranickel showed any promise. Although Hastelloy D is difficult to fabricate because of its 10 wt% silicon, it was used in several pilot plant runs in the PbCl_2 -KCl system because in corrosion tests it showed no accelerated interfacial attack. Corrosion of Hastelloy D in LiCl-KCl proved to be too great even for short-term experiments. Duranickel was tested in one pilot plant run in the PbCl_2 -KCl system with an interface protected with graphite. High corrosion rates resulted. Corrosion of the cathode always adversely affected the crystal structure of the deposited UO_2 . As typical example of this problem, Figure 36 shows a nickel cathode used in LiCl-KCl. The crystal size is greatly reduced by corrosion beneath the deposit.

FIGURE 36
Effect of Corrosion of Nickel Electrode on UO_2 Deposit

Graphite Cathodes

Although reactor-grade graphite had adequate chemical resistance for use as cathodes, the porosity of the surface caused mechanical interlocking that resulted in gross carbon contamination of the UO_2 . Although this contamination was highly variable as can be seen from Tables VIII, IX, X, XII, and XV (pages 42, 55, 63, 67, and 89, respectively), the carbon content was often at least 500 ppm.

Hammers and wedges were used to chip the deposits off the flat cathodes in early pilot plant runs, but the round cathodes employed in the hot cell could not be handled in this way. In one attempt at removal, a die that was slightly larger than the 1.5-in.-diam electrode was forced along the electrode. Because the UO_2 is both stronger and harder than the graphite, appreciable carbon was scraped off by the die. Centering problems were aggravated any time the die began to cut the soft carbon on one side of the electrode. Nevertheless, as shown in Table XIV (page 80), the bulk UO_2 in the prototype runs had carbon contents as low as 100 ppm.

For remote operations a wedge mounted in a hydraulic press, shown in Figure 37, was used to split the UO_2 deposit from the cathode. A thin

FIGURE 37
Electrode Stripping Apparatus

pyrolytic graphite coating was applied to the pile graphite.* As shown in the plane-polarized light photograph in Figure 38, a pyrolytic graphite coating of only 0.25 mil thickness was sufficient to seal the pores of the surface of the electrode. The application of this coating produced immediate success in

Plane-Polarized Light

FIGURE 38

Pyrolytic Graphite Coating on a Pile Graphite Cathode

separating the UO_2 from the cathode (Figure 39). The wedge split the untreated cathode with essentially no separation of UO_2 from carbon, while the UO_2 split off the pyrolytic graphite cathode cleanly without affecting the coating. Analysis of the product shown in Table XII (page 67) gave carbon contents consistently below 50 ppm. The carbon content of the 1/16-inch-thick layer of UO_2 nearest the cathode was about 50 ppm with lower values in the bulk UO_2 . Tests showed that the pyrolytic graphite cathodes could be used again many times. Pyrolytic graphite cathodes were used exclusively in the Salt Cycle demonstration and proved to be remotely separable from the deposits in all runs.

There is appreciable incentive to use pyrolytic graphite for anodes also, since laboratory studies have shown it has less tendency to corrode and to react with the chlorine to form U(IV) .⁽⁶⁾ Whether this is due to decreased

* Pyrolytic graphite coating was performed by the Metallurgical Products Dept. of the General Electric Company, Detroit, Michigan and by High Temperature Materials, Inc., Boston, Massachusetts.

FIGURE 39
Comparison of Stripping of UO_2 from Pyrolytic-Graphite-Coated Electrode with Stripping of a
Pile Graphite Electrode

electrode surface area, increased mechanical stability of the surface under slight corrosion, or chemical inactivity is not yet known.

CONTAINER EVALUATION

The Salt Cycle environment is a particularly harsh one for metallic materials of construction. The presence of wet chlorine and hydrogen chloride in the off-gas from the salt bath precludes the use of stainless steel, even at room temperature. Fortunately, as is shown in Figure 40, the temperatures in the pilot plant equipment used in the Salt Cycle demonstration⁽⁷⁾ were low enough so that nickel, Hastelloy B and Hastelloy C could be used in contact with the gas in the dual lid and in the off-gas lines. The susceptor in contact with chlorine gas at temperatures above 600 °C was made of Hastelloy B and held up for several months if no salt contacted it.

Metallic Crucible Materials

The search for metallic crucibles began during the pilot plant operations in the NaCl system and was continued throughout operations in the other salt systems. An evaluation of metallic materials in the NaCl-KCl system by Battelle-Columbus⁽³¹⁾ showed corrosion rates to be excessive, but pointed toward nickel-aluminum alloys as the best potential material. Further work was done in the other salt systems by W. L. Walker⁽³²⁾ at Hanford Laboratories. The corrosion rates on a few of the materials used in Walker's studies are shown in Table XVII. Attack on metals at the gas-liquid interface was usually accelerated. Corrosion in the LiCl-KCl system at 600 °C was more rapid in some cases than in the NaCl-KCl system at 800 °C. The nickel-aluminum alloys, though brittle, showed great promise in LiCl-KCl but the corrosion rates were increased by at least a factor of ten by adding UO_2Cl_2 . Further work on varying compositions of these alloys with additives of other elements might prove fruitful, although the addition of chromium, for example, increased corrosion.

Fused Silica Crucibles

Fused silica vessels are satisfactory from a corrosion standpoint but are very brittle. Furthermore, in the pilot plant a frozen salt bath cannot be reheated without breaking the crucible. In the NaCl-KCl system, the frozen salt

FIGURE 40
Temperature Profiles in the Salt Bath Mockup for the Salt Cycle
Demonstration

TABLE XVII

CORROSION OF METALS IN THE SALT CYCLE ENVIRONMENT

All exposures are single periods of about six hours, with a single sample exposed in a manner which resulted in approximately equal areas in the liquid and vapor phases. All systems were sparged at a rate of about 300 ml/min.

Corrosion rates were calculated from weight losses, and represent an average rate over the entire sample. In most cases this average rate is considerably lower than the maximum rate at some point on the sample.

Systems

1. Equimolar NaCl-KCl - 750 to 800 °C - HCl sparge
2. 60 wt% PbCl₂-40 wt% KCl - 600 °C - Cl₂ sparge
3. 40 wt% LiCl-60 wt% KCl - 600 °C - HCl sparge
4. 40 wt% LiCl-60 wt% KCl - 600 °C - Cl₂ sparge

Alloy	System			
	1	2	3	4
(All rates in mils per month)				
Hastelloy B	84 I	930 I	94 I	740 I & L
Hastelloy C	195 I	1250 I	105 V	815 I
Hastelloy D	195 I	840 V	56	805 I & V
Inconel	460 V	206 I		
Inconel X	625 V & L	262 L		
Inconel 702	190 V	82 I	95 I	127 I
"A" Nickel	670	129 I	54 I	73 I
Permanickel	210 L	139 I		143 I & L
Duranickel	140 L	27	84 I	58
Tungsten	80 V			98 V
Hastelloy N (INOR-8)	390 I	680 I		
Platinum	3 I*			390 I
Molybdenum	113			
Tantalum	730 V	1000 L		
Niobium	1100 I			
Titanium - 0.2 wt% Pd	> 2000		> 2000	
Duriron	300			
Durichlor	700 V			

Special Alloys

BMI #15 (Ni-13 Al)	nil		5 (63**)
BMI #3 (Ni-15 Al)	3		3 (64**)
BMI #16 (Ni-43 Al)	wt gain***		
Ni ₃ Al (12.5 wt% Al)			5
NiAl			2 (83**)
Ni-12.5 at.% Al-12.5 at.% Cr			180

V - Accelerated attack in vapor phase.

I - Accelerated attack at interface.

L - Accelerated attack in liquid phase.

Samples not designated with a letter exhibited relatively uniform corrosion.

*Sample exhibited an interface pitting rate of > 1000 mpm.

**Corrosion rate in presence of 10 wt% UO₂Cl₂.

***Sample is porous and salt penetrated completely through 1/4 in. thickness.

shrank enough so that it could be removed from the crucible in one piece and the crucible could be reused. Reheating with salt in place always broke the crucible. In the PbCl_2 -KCl and LiCl-KCl systems the salt could not be removed after freezing and the only way the crucible could be saved was by vacuum transfer of the salt into another container. The most critical point in the life of a crucible is at startup when fresh salt is being added and melted down until the vessel is full. Indefinitely-long crucible lifetimes are possible with steady-state operation at molten salt temperatures.

The durability of the quartz vessels when properly handled is illustrated by an 18-in. diam vessel used in the 80 liter pilot plant runs. The vessel was operated at 550 to 600 °C during Runs LK 26 thru 29. Then the molten salt was vacuum transferred to a steel container where it was frozen and broken up into pieces. The same vessel was then reused with the same salt for a total operating time of 148 days. Examination of the crucible after the salt had been pumped out showed spalling of the bottom, where the salt may have frozen because of heat losses through the bottom at the lowest operating temperature (535 °C). Similar experience was noted in the hot cell prototype operation during which a vessel lasted for seven months before being shut down at the end of the program. Vessel lifetimes in the Salt Cycle demonstration where remote handling was necessary were also long. ⁽⁷⁾

Fused Silica Vessel Failures

If a fused silica crucible breaks, the salt corrodes through the susceptor within one day, but then the salt is imbibed by the insulation around the vessel and a frozen wall is formed. Figure 41 shows a 6-in. diam induction heated system that was operated 50 days before the silica pot broke on heating up after being frozen by a heater shutdown. The equipment was then operated for 66 hours at 600 to 735 °C with the salt penetrating to the outside of the insulation where it remained molten in some spots but was held in the insulation by a wick effect. Twenty-liter vessels were operated in the same way without salt penetrating the insulation. The contents of the vessel were difficult to recover even though safe operation was always maintained.

FIGURE 41
Induction-Heated System After Several Days Operation with a Broken
Quartz Crucible

Other Nonmetallic Materials

Other nonmetallic crucibles were evaluated by J. H. Kleinpeter⁽³³⁾ to find a material that could be frozen and reheated with the salt remaining in the crucible. Most materials tested leaked salt when held at temperature for long periods. Only high density alumina did not leak salt and its mechanical properties were no better than those of quartz.

Frozen Wall Systems

Systems with internal alternating current heating and metallic walls covered with frozen salt^(34,35) were tested. Although the heat losses were too high to permit flexible operation because of the small system size, the 60-cycle AC heating could be introduced with the same electrodes used in the electrolysis without adversely affecting the deposition of UO_2 . These systems were never used in the pilot plant because the solids being dissolved

would inevitably end up in the frozen wall. This was intolerable since criticality control of plutonium was on a batch basis.

A promising frozen wall system is the one shown in Figure 42, which had an induction-heated graphite susceptor surrounded by sand inside a Transite pipe. After five days' operation at 550 °C with LiCl-KCl (including thermal cycling) an apparently stationary frozen wall was found about 1/4-in. into the sand outside the graphite and there was no cracking of the 3/4-in. graphite wall. Tests with graphite crucibles had previously shown that the salt leaked through the graphite in less than 24 hr.

FIGURE 42

Cross Section of a Graphite Susceptor with a Frozen Wall After Several Days Operation

A similar apparatus was operated without the sand, but with a 15 psig gas pressure outside the susceptor. Although gas leaked into the crucible, salt did not leak out and stable operation was achieved.

A porous graphite crucible impregnated by barium chloride was tested in LiCl at 500 °C. In about five days the salt leached through the 3/4-in.-thick wall and flowed out of the crucible.

Pyrolytic-Graphite-Coated Crucibles

Two graphite crucibles coated with pyrolytic graphite tested in LiCl-KCl at 550 to 600 °C are shown in Figure 43. The coating was only a few mils thick on the inside of the crucible but pyrolytic graphite impregnation to at least 50 mils was obtained in the manufacturing process.* The first crucible was tested for 13 days with 2 thermal cycles to room temperature. No penetration of the crucible by the salt was detected but the air atmosphere had severely corroded the vapor space. The second crucible was operated for 13 days with an argon atmosphere and 3 thermal cycles. The crucible was apparently in perfect condition and the frozen salt block was readily removed, indicating no penetration of the wall by salt.

Although pyrolytic-graphite-coated crucibles appear to have the impermeability and mechanical strength necessary for a molten salt crucible, the chemical reactivity of graphite in the LiCl-KCl- UO_2Cl_2 -chlorine system shown in the Salt Cycle demonstration⁽⁷⁾ makes further tests necessary to demonstrate their usefulness.

CODEPOSITION AND PARTITION

The eventual feasibility of the Salt Cycle process is dependent upon the plutonium behavior during electrodeposition. Maintaining the plutonium in its lowest valence state while electrodepositing stoichiometric UO_2 is relatively simple. If the bath has been dried sufficiently, a hydrogen chloride or chlorine gas sparge will reduce the plutonium to Pu(III) or Pu(IV) and prevent it from codepositing with the UO_2 . Codeposition of UO_2 and PuO_2 , on the other hand, is more difficult because the oxidizing conditions required to produce Pu(VI) might not be suitable for producing stoichiometric UO_2 and Pu(VI) might be reduced in solution near the cathode without depositing. The production of nonstoichiometric UO_2 in itself, while not desirable, is not intolerable because the mixed oxide product can be hydrogen-reduced. However, if the oxygen-to-uranium ratio is higher than 2.1, a porous deposit will result and high density fuel elements will not be possible.

* These crucibles were produced by the Metallurgical Products Dept. of the General Electric Company, Detroit Michigan.

In an Air Atmosphere

In an Argon Atmosphere

FIGURE 43
Pyrolytic Graphite Crucibles After Testing at 600 °C for 13 Days

Since the pilot plant facility was not equipped to handle the contamination from plutonium, a series of tests was conducted with cerium stand-in for plutonium. At the time of the tests cerium was believed to behave more closely to plutonium in codeposition than any other element because of its potential ability to be oxidized from a relatively stable Ce(III) state to a relatively unstable Ce(IV) state by chlorine-air mixtures. Later hot cell experience in the Salt Cycle demonstration⁽⁷⁾ surprisingly showed that the behavior of the trivalent rare earths yttrium and europium was much closer than to that of plutonium, and that DF's of 10 could be obtained for cerium in codeposition of plutonium with uranium.

Cerium Stand-In for Plutonium

The cerium stand-in runs are summarized in Table XVIII. A salt charge of about 6 kg was made up to the composition equimolar LiCl-KCl, 20 wt% uranium and 1 wt% cerium. The uranium was introduced as $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ and the cerium was introduced as $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. Cerium-144 tracer was added as 10 ml of aqueous solution. The bath was sparged with hydrogen chloride gas until dry by the microelectrode test (page 51). Electrolyses were conducted at 1.5 V and 530 °C with about 25% of the uranium deposited in each run. Material balances on the tracer were poor; as much as half of it was lost, but the material balances on the bulk cerium were good.

Runs CTC-1 and CTC-2 show that either hydrogen chloride or chlorine sparges could prevent cerium from codepositing with the UO_2 with a decontamination factor of 15 to 20. A 50 vol% chlorine-50 vol% air sparge produced a cerium DF less than 5, and an oxygen-to-uranium ratio less than 2.01. Figure 44 shows the type of deposit produced under these conditions, which eventually proved to be the best for codepositing PuO_2 with UO_2 in the Salt Cycle demonstration.^(6,7) An air sparge also produced low cerium DF's as shown in Runs CTC-4 and CTC-6 but resulted in high O/U ratios up to 2.08. An attempt at continuously dissolving U_3O_8 , by placing the U_3O_8 in a hollow graphite anode with holes drilled in it, resulted in a deposit with a low cerium DF and a high oxygen-to-uranium ratio. An electrolysis with a chlorine sparge that had been bubbled through water also produced a high O/U ratio and a low cerium DF. In a high temperature (700 °C) partition electrolysis the graphite anodes were corroded

TABLE XVIII

CERIUM STAND-IN FOR PLUTONIUM IN UO₂ DEPOSITION

Run No.	Electrolysis Condition	Feed to Deposit Cerium Decontamination Factor		Oxygen to Uranium Ratio		9μ Density	
		Tracer Analysis	Chemical Analysis	As Deposited	After Reduction	As Deposited	After Reduction
CTC-1	HCl sparge	22.9	20.1	2.0024	---	10.777	---
CTC-2	Chlorine sparge	14.1	14.1	2.0058	---	10.546	---
CTC-3	50 vol% Cl ₂ - 50 vol% air sparge	4.2	4.8	2.0066	---	10.849, 10.890*	---
CTC-4	Air sparge	1.66, 2.55*	4.3, 9.3*	2.0777, 2.0202*	2.0021	10.541, 10.891*	10.781
CTC-5	U ₃ O ₈ basket anode, no sparge	1.86	9.3, 13.9	2.060	2.0016	10.893	10.807
CTC-6	Air sparge	1.1, 1.5*	4.5, 7.6*	2.0304, 2.0079*	---	10,772, 10,771*	---
CTC-11	Wet chlorine sparge	2.9	2.8	2.0622	2.0162	---	---
CTC-12	High temperature partition	---	---	2.0019	---	10.621	---
<u>Intermittent Electrolyses</u>							
CTC-7	Cl ₂ sparge	23.6	> 22	2.0048	---	10.813	---
CTC-9	50 vol% Cl ₂ - 50 vol% air sparge	1.2	5.3	2.0714	2.0059	10.911	---
CTC-10	Air sparge	3.0	3.7	2.1520	2.0585	---	10.192

*Side away from the sparge

Electrolyses were conducted at 530 °C in equimolar LiCl-KCl with 20 wt% U and 1 wt% Ce in initial melt. About 25% of the UO₂ was deposited in each run.

106

B777-354

CTC-3 Growing Surface

0.2"

CTC-3 Cross Section

FIGURE 44
Codeposit with 50% Oxygen - 50% Chlorine Sparge

off at the liquid-gas interface by air entering the vapor space. The cerium DF in this run was high and the UO_2 produced was compact and crystalline (Figure 45).

An attempt to increase the quantity of Ce(IV) in solution was made by electrolyzing intermittently with the current alternately on for one minute and off one minute. The oxidizing gases increased the O/U ratio of the product much more with an intermittent electrolysis, but the cerium DF was not significantly affected. The crystal structure is a stronger function of sparge gas used than with continuous electrolyses, as shown in Figure 46. The on-off cycles are easily visible in the deposit from Run CTC-7. Hydrogen reduction of the CTC-9 product with an O/U ratio of 2.07 was accomplished without significantly changing the crystal structure and the density. The product of Run CTC-11 with air sparging is clearly unsuitable for making -4 + 10 mesh particles.

Codeposition of Nickel- UO_2 Cermet

During the preliminary experiments in the hot cell before startup of the Salt Cycle demonstration, an electrolysis was performed in a LiCl-KCl salt bath containing uranium, plutonium and products of corrosion of a Hastelloy B susceptor. The fused silica vessel had broken a few days before the electrolysis and appreciable nickel was dissolved in the bath. The salt before electrolysis contained 0.84 wt% U, 1.6 wt% Ni and 0.04 wt% Pu. The electrolysis was conducted at 530 °C with graphite electrodes at 2.0 V and 1.7 amp/in.² current density at the cathode with a 50% Cl_2 -50% O_2 gas sparge. After electrolysis the salt contained 1.0 wt% U (an increase!) and 0.021 wt% Ni. Analysis of the product by weight gave 0.52% Pu, 65% Ni, 29.6% U, 2.2% Mo, 0.12% Fe, 0.33% Cl, 0.04% Li, and an O/U ratio of 2.094. Examination of photomicrographs of the product showed it to be a probable mixture of nickel metal and UO_2 with appreciable dispersion of UO_2 in a nickel matrix. The nickel tended to be continuous and filament-like, containing globules of UO_2 . The deposit was very porous and not macroscopically homogeneous, with the nickel concentrated at the inner and outer surfaces of the deposit. The results of this experiment do not seem to agree with the results shown in Table XIII (page 77) in which very high nickel decontamination factors were

CTC-12 Growing Surface

0.2"

CTC-12 Cross Section

FIGURE 45
Deposit from a High Temperature Partition

Chlorine Sparge

Run CTC-7

0.2"

Chlorine-Air Sparge

Run CTC-9

Air Sparge

Run CTC-10

FIGURE 46
Codeposits with Intermittent Electrolyses

obtained, although the operating conditions were somewhat different. Further work might result in the development of a method for producing UO_2 or $\text{UO}_2\text{-PuO}_2$ cermet that are suitable for use as nuclear fuels.

PRECIPITATION

Several flowsheets for the Salt Cycle process include precipitation of plutonium from the molten salt as a means for producing a dense, crystalline PuO_2 product directly or as a step for achieving the necessary rare earth decontamination factors for a codeposited, mixed $\text{UO}_2\text{-PuO}_2$ product. Since plutonium could not be used in the development facility, cerium and thorium were used as stand-ins. The means for recovery of the precipitate from the vessel was studied rather than the formation of the precipitate because the PuO_2 immediately forms an easily filterable precipitate,⁽⁶⁾ and because the chemical behavior of cerium and thorium are somewhat different from that of plutonium in molten salts.

Freeze-Valve Technique

A freeze-valve technique was tested briefly to remove precipitate from the molten salt bath. The quartz vessel had an open quartz tube extending through the bottom of the induction furnace into a separately controlled heating zone. The molten salt fills this tube and is allowed to freeze, sealing the bottom of the vessel. The molten salt can be drained from the vessel by melting the salt plug in the tube. It then passes through a quartz frit filter, and the precipitate is recovered by aqueous washing after the filter cools. The frozen salt plug is reestablished after incremental quantities of molten salt have been drained from the vessel. Only two tests were conducted with this apparatus. In the first test the frozen plug was established below a vessel containing a UO_2 slurry. The plug was then melted, draining the vessel and collecting the UO_2 on a quartz frit. The second test resulted in breakage of the quartz tube during melting of the frozen plug.

Thorium Stand-In for Plutonium

Thorium was a poor stand-in for plutonium in the study of PuO_2 precipitation procedures from the 2.5 LiCl-KCl molten salt system. Good precipitation of thorium was not achieved because the ThO_2 formed a slurry rather than

settling rapidly as does PuO_2 . A 40% O_2 -60% Cl_2 reactant gas mixture was contacted through a filter of -50 + 100 mesh quartz sand for 7 hr at 570 °C with a recovery of only 5% of the thorium on the filter. Material balances indicated that 50% of the thorium was precipitated as ThO_2 , and therefore the filter efficiency was about 10%.

Cerium Stand-In for Plutonium

Equipment for the recovery of plutonium as PuO_2 from a molten LiCl-KCl salt solution by treatment with oxygen-chlorine was tested using cerium as a stand-in for plutonium. The cerium was precipitated from a 2.5 LiCl-KCl mixture containing 10 wt% U and 0.63 wt% Ce by gas-lifting with a 60% Cl_2 -40% O_2 gas mixture through a filter assembly. The filter assembly consisted of three 30 mm diam quartz-tube chambers with quartz-frit bottoms through which the molten salt cascaded in series, finally overflowing the third chamber. The CeO_2 precipitate settled in all the chambers and adhered to the quartz tubing and frits. Approximately 50% of the precipitate was recovered with the above filter arrangement; however, since only 24% of the cerium was precipitated, a good test of the filter arrangement was not obtained. The precipitate was crystalline and black in color and did not form a stable suspension in either water or the molten salt as did ThO_2 . The cascading filter apparatus failed after three runs because of cracks apparently caused by attack on the quartz by the chlorine-oxygen, fused-salt mixture. Bonding of the CeO_2 precipitate to the quartz may also have promoted weakening of the quartz.

A recirculating gas lift was tested at 580 °C to determine how much CeO_2 could be collected on this piece of equipment alone. The gas lift consisted of two concentric pieces of quartz, 51 mm and 10 mm in diameter, the 51 mm tube tapered to a 20 mm opening at the bottom. Gas was admitted through the 10 mm tube. A 24-hr 70% O_2 -30% Cl_2 treatment resulted in precipitation of 85% of the cerium and recovery of 43% of the cerium on the apparatus. Most of the recovered CeO_2 was deposited on the sloping surface where the 51 mm tube narrowed to a 20 mm opening and was removed by soaking in 0.5M HNO_3 .

Direct precipitation of CeO_2 on the bottom of the vessel by sparging was followed by gas lifting of the salt through a filter to recover the precipitate. Comparison of the CeO_2 precipitation experiments with previous work on plutonium⁽⁶⁾ showed that 80% of the cerium would be precipitated as CeO_2 under the same conditions for which greater than 90% of the Pu had been precipitated as PuO_2 . However, operation for 23 hr with a 50% Cl_2 -50% O_2 gas lift precipitated only 60% of the cerium. A graphite filter was substituted for the usual quartz assembly with the result that only 8% of the cerium was precipitated after the 23-hr 50% Cl_2 -50% O_2 gas lift treatment. Attack on the graphite was noted, indicating a possible redissolution of the CeO_2 by reaction with chlorine and carbon.

The tenacious adherence of CeO_2 and PuO_2 to the quartz suggested the use of a high porosity filter consisting of a quartz Gooch crucible filled with large quartz chips to pick up the CeO_2 . With this apparatus a 60% O_2 -40% Cl_2 sparge through the gas lift precipitated 90% of the cerium, and about 70% of that precipitate was recovered on the filter and the gas lift. The CeO_2 was removed from the quartz by washing in 8M HNO_3 -0.2M HF solution. A 10 wt% NaOH solution was also found to be effective for removal. The success of only these methods indicates that the CeO_2 is removed only by attack on the quartz. A sieve analysis of the product yielded 10% +100 mesh and 56% -100 + 200 mesh particles. X-ray analysis of the CeO_2 product showed that the precipitate from a 2.5 LiCl-KCl mixture containing 10 wt% U and 0.63 wt% Ce was comprised of 91% CeO_2 and 9% UO_2 as a solid solution with diffraction lines of CeO_2 . Breakage caused by quartz corrosion during CeO_2 precipitation made it necessary to replace the filter apparatus after two runs.

In all, six precipitation runs were made in the 20 liter salt bath containing 2.5 LiCl:1 KCl molten salt. Of the various recirculation devices designed to collect the CeO_2 which were operated with a Cl_2 - O_2 sparge, the design that gave the best recovery (65%) was the simple bed of quartz chips through which the molten salt was circulated. An overall analysis of the six runs showed that 248 g of cerium were recovered, and 32 g of cerium remained in solution. This means that 110 g of cerium was lost, probably by plating of the cerium on the quartz pot above the surface of the molten salt solution.

A large quantity of black material ($\text{CeO}_2\text{-UO}_2$) was visible at this location. This plating problem would not be as acute in the 1:1 KCl-LiCl system, although the precipitation itself also would not be as complete.

The chief difficulty in all the tests was the precipitation of CeO_2 and probably PuO_2 as later shown in the Salt Cycle demonstration,⁽⁷⁾ on surfaces where it was not desired. Experiments with a graphite liner were conducted to prevent precipitation of CeO_2 on the quartz vessel walls. This was apparently successful in short term tests, but the chlorine-oxygen atmosphere produced severe corrosion during several weeks of operation. Possibly, a chlorine-oxygen gas lift operating in this system would recover more precipitate on the filter than in unlined vessels.

CRUSHING AND SIEVING

To demonstrate recycle of fuel to the reactor, it was necessary to develop remotely operable equipment to produce mixed oxide of the proper particle size for vibratory compaction. A goal was set to develop equipment to produce a UO_2 product with 60% -4 + 10 mesh, 20% -35 + 65 mesh, and 20% -200 mesh particles, a 3-size mix which was ideally suited for vibratory compaction.

Early work was done with a wet crushing and screening system because of the possibility of scattering radioactive dust about the cell in dry methods. However, its development was not far enough along to guarantee success in the Salt Cycle demonstration with the time schedule available. An Iler[®] Disc Pulverizer with eccentric rotating discs was evaluated and met the product specifications, but there was not room enough to put it in the hot cell and there was some doubt whether it could be operated remotely. Further tests were conducted with a press-type crusher which could also be used to strip oxide from the electrodes and to cut up cladding for disposal. This proved suitable for producing the coarse and intermediate size fractions. A multi-purpose pulverizer was also developed to produce the fines fraction, sieve the product, and blend the size fractions together. However, a separate sieve shaker and ball milling of the fines were eventually selected for use in the Salt Cycle demonstration.⁽⁷⁾

[®]The Fen Machine Company, Wickliffe, Ohio

Wet Crushing and Sieving System

An integrated system was assembled and operated to study remote crushing, screening, and washing of electrolytically-deposited UO_2 in a completely wet system. The equipment shown in Figure 47 contained the following major components:

1. A motor-driven single-roll crusher consisting of four 4-in.-diam, staggered-tooth milling cutters mounted on a keyed shaft. Fixed-clearance grate bars (1/8-in.) blocked passage of oversize particles.
2. A double-deck Novo* screen, with two flat, inclined screens driven by an electromagnetic coil. Four screens were used in two combinations: 3 and 30 mesh, and 100 and 200 mesh.
3. A closed loop washing system consisting of a wash column, a pump and a 3-in.-diam x 12-in.-long hydroclone, the underflow of which fed the screen.

During operation of the system, 2- to 3-in.-long slabs of UO_2 are fed to the crusher and pulverized particles are dropped through to the wash column below. By closing the crusher discharge valve and throttling the pump discharge, the particles are washed by an upward moving stream of water. Increasing the water flow fluidizes the UO_2 , carrying particles to the screen for classification. Processing 150 lb of UO_2 in the integrated system gave satisfactory performance except as noted below.

With 1/8-in. grate bar clearance a typical product consisted of 60% -6 + 30 mesh, 95% -3 + 200 mesh, and 5% -200 mesh particles. The product could be coarsened by increasing grate bar clearance, but the narrow particle size ranges desired for fuel refabrication were not achieved in these studies.

Good classification of -200 mesh particles was not achieved in the wet system, particularly when using the 200 mesh screen. As a result, the finer particles tended to become distributed throughout the system. In general, hydraulic transport of crushed UO_2 appears to offer advantages of good dust control, process flexibility, and contamination control, particularly if washing is required as a normal part of the process. However, the relatively large volumes of water required may be objectionable.

* Novo Industrial Corp., Chicago, Illinois.

FIGURE 47
Wet Crushing and Sieving System

Iler Disc Pulverizer

The disc pulverizer has one fixed and one rotating disc as is shown in Figure 48. The fixed disc oscillates against the revolving disc in a vertical motion. The degree of fineness of the product is regulated by manually rotating the shaft guide for the rotating disc to change the gap between the discs.

FIGURE 48
Iler Disc Pulverizer

A calibration of the apparatus for electrolytic UO_2 at 557 rpm with a choke feed is given in Figure 49. The numbered settings are arbitrary and will vary with the machine and the numbering system used. For electrolytic UO_2 a No. 41 setting gives 3-mesh particles and a No. 25 setting gives 8-mesh particles,

FIGURE 49
 Variation of Gap Between Discs - Product from Iler Disc Pulverizer

using the 50% mass fraction as an indicator. Less than 200-mesh particles can be obtained with very fine settings. Changing from choke feeds with the hopper full of 1/2-in. to 3/4-in. chunks to single particle feed increased the median particle size by 1.4 times for approximately 20-mesh product but did not alter the sharpness of the size distribution significantly.

The most difficult part of achieving the desired particle size distribution is to get the largest fraction of the product in the relatively narrow size range $-4 + 10$ mesh. Reducing the speed of the crusher from the standard 557 rpm to 40 rpm greatly sharpens the peak of the size distribution as is shown in Figures 50 and 51. Further speed reduction to 7.8 rpm has little effect. Nonreproducibility of feed material is also a strong factor in the product obtained. Although the UO_2 products of electrolysis Runs HS-8 and HS-5 appear to be nearly identical in all other ways, the HS-8 material clearly degrades more easily and does not produce a narrow size range product. A second characteristic of HS-8 product which is not due to the disc pulverizer is the appearance of a secondary peak at 35 mesh. This peak occurred only at the finer No. 18 setting and is reproducible. From the results of the screening of the NaCl-KCl product (Figure 17, page 44), it is known that such secondary peaks may be due to the presence of agglomerates of this size crystal in the as-despoited UO_2 , which break down on crushing. Microscopic examination of the deposits show that such agglomerates tend to form in the first layer of UO_2 deposited, near the electrode in wet or impure melts. Since this secondary peak is very close to the size of the desired intermediate particle size, control of the size and location of this peak could greatly simplify required crushing operations.

Moisture will be present in the UO_2 if the deposit is not stored in a dry atmosphere because the lithium chloride in the adherent and occluded salt is hygroscopic. The effect of moisture picked up by LiCl on crushing and screening operations is shown in Figure 52. The fine particles below 30 mesh agglomerate, producing a characteristic step in the particle size distribution curve. Agglomeration of fines is desirable to reduce radioactive dust formation, but fines adhering to larger particles could alter the size distribution in the final mix, and corrosion of the screens by aqueous chlorides is detrimental. Immediate drying and rescreening deagglomerates the fines and results

FIGURE 50
 Effect of Speed on Crushing with Iler Disc Pulverizer - Coarse Setting

FIGURE 51
Effect of Speed on Single Pass Crushing of Electrolytic UO_2 with Iler Disc Pulverizer

FIGURE 52
Effect of Moisture on Crushing and Screening Operations with Iler Disc Pulverizer

in a slight lowering of the peak, which could be due to degradation of the -6 + 8 mesh particles or loosening of fines stuck to large particles. Washing and drying the product before crushing lowers the peak appreciable and produces more fines. This may be related to fracturing of large particles during drying, or greater particle degradation during dry crushing.

The results of crushing the UO_2 in several size reduction steps are shown in Figure 53. The significant conditions for these runs are HS-8 feed and 557 rpm, which should be compared with the single Run 1C-17 in Figure 51, which produced 38.8% -4 + 10 mesh product. Decreasing the feed-to-product size-reduction ratio per step and using only the +4 mesh material as feed for the next step produced a combined product containing 49.7% -4 + 10 mesh, which is far greater than any single stage crushing operation could produce with this feed material and crusher speed.

Press Crushing with Notched Blades

Earlier experiments with a Carver* hydraulic press had shown that the UO_2 could be split off pyrolytic graphite electrodes by a single V-shaped blade (Figure 37, page 94). Since the hot cell demonstration would require only a very low capacity crushing apparatus and the development of multi-purpose equipment was desirable because of space considerations, size reduction by pressing was studied. The test apparatus is shown in Figure 54. The pressures reported are those read on the press gauge, so that they must be related to the area of contact, which was about 10 in.², to indicate the crushing force directly.

Cutting the large as-deposited UO_2 chunks into 1/2-in. cubes with a single blade 5/8-in.-deep x 5/8-in.-wide triangular cross section was accomplished with very little fines formation as shown in Figure 55. This was made easier because deposits are usually about 1/2-in. thick so that only cutting along the crystal boundaries is required. Three 5/8-in. blades produced the same distribution when operated without overloading. Crushing of large pieces of UO_2 with three parallel blades at 5/16-in. spacing produced a size distribution peak at -3/8-in. + 3 mesh, but appreciable fines were produced. Use of 5/32-in. blades produced a peak in the desired -4 + 10 mesh range but

* Fred S. Carver, Inc., Summit, New Jersey.

FIGURE 53
Integrated Crushing of Electrolytic UO_2 with Iler Disc Pulverizer to Produce Large Size Fraction

FIGURE 54
Press for Dicing and Parallel Plate Crushing Tests

FIGURE 55
Product from UO_2 Dicer Operation at 500 psi Terminal Pressure

even more fines were produced, probably because the pieces were always crushed a little after the blades had split them since no dimension of the original piece was less than the blade depth.

In Figure 56 is shown the effect of pressure on an integrated dicing operation. The $+4$ mesh material from each test was used as feed for the next smaller set of blades. Lowering the gauge pressure from 500 psi to 200 psi increased the desired $-4 + 10$ mesh fraction from 50 to 53% and decreased the -65 mesh fines threefold from 7.2% to 2.8%. A check on the reproducibility of tandem dicing operations gave little variation in duplicated operations.

In Figure 57 the contributions of the products from each blade size in a tandem series of 4 dicings are shown. The 5/16 in. and the 5/32 in. blade dicing steps produced 35.0 and 33.8%, respectively, of their products in the $-4 + 10$ mesh range compared with 21.8% in the single step dicing shown with 5/16 in. blades in Figure 55. The total percentage of $-4 + 10$ mesh in the composite product was 56.2%, quite close to the goal of 60%, but the intermediate $-35 + 65$ mesh fraction was only 12.0%, far less than the desired 20%.

Parallel Plate Crushing

Although dicing was found to be feasible for producing the largest particle size fraction, it could not produce the required quantity of the $-35 + 65$ mesh fraction. Roll crushing appeared to be a reasonable alternative not only for the intermediate fraction but also for the large size fraction after initial dicing to $-3/4$ in. $+ 1/2$ in. chunks had been accomplished. Because the space limitations required multipurpose equipment, the hydraulic press with parallel plates was tested as a substitute for roll crushing. In view of the beneficial effect of speed reduction on the Iler disc pulverizer performance, parallel plate crushing considered as zero speed roll crushing appeared attractive.

In parallel plate crushing the bottom plate is recessed to eliminate indexing the plate spacing by controlling the throw of the hydraulic power supply. The recess is filled with particles to be crushed and the desired pressure is exerted by the press. Figure 58 shows two important factors influencing the product particle size distribution ratio. Increasing the step

FIGURE 56
Effect of Pressure on Dicing of Electrolytic UO_2

FIGURE 57
Production of Large and Intermediate Size Particles by Integrated Dicing Operations
Comparison of Size Distribution with Iler Disc Pulverizer Product

FIGURE 58
Single Pass Crushing with Parallel Plates
Effect of Step Size and Size Reduction

size from 0.125 in. to 0.156 in. increases the product particle size by a factor of 1.5. At the same time, increasing the size of the feed spreads the distribution of the product particles and produces more fines. A gauge pressure of 10,000 psi or greater was used in all parallel plate crushing runs.

The effect of batch size upon the particle size distribution is shown in Figure 59. If a single particle were crushed there would be no interaction between particles and a minimum of fines is produced. The effect of doubling and redoubling the batch size is to decrease the peak height, to shift it slightly to lower particle size, and to increase the quantity of fines. The middle batch size of 57 g per crushing pass was used in most parallel plate crushing studies.

The last stage in the procedure for optimizing the step sizes to be used in tandem crushing with parallel plates is shown in Figure 60. In this stage the 0.156 in. step is selected over the 0.222 in. step as the fourth part of a five part series to produce a -4 + 10 mesh particle. The 0.156 in. step shows an increase in the large size fraction from 56.4% to 63.4% and with a corresponding reduction in the -65 mesh fines.

The next problem was to develop a method for converting as much as possible of -10 + 35 mesh fraction to -35 + 65 mesh. As shown in Figure 61, both 0.016 in. steps and 0.012 in. steps were tried with 10,000 psi pressure but the resulting peak was at too large a particle size. A higher pressure of 16,000 psi and no step gave the highest fraction, 43.7% in the desired range. The Iler Disc Pulverizer is also capable of producing a product in the desired range. At the optimum setting of 3.5, about 48% of the product is in the -35 + 65 mesh range.

The final treatment scheme selected for use in the Salt Cycle demonstration is shown in Figure 62. As employed here it produced 57.5% -4 + 10 particles, 19.7% -35 + 46 mesh particles and all other fractions were pulverized to -200 mesh by ball milling.

Multipurpose Fines Production, Sieving, and Blending Equipment

Because of space limitations in the Salt Cycle demonstration, development of a single, multipurpose apparatus for producing minus 200 mesh fines, sieving

FIGURE 59
Effect of Batch Size on Parallel Plate Crushing

FIGURE 60
 Integrated Parallel Plate Crushing of Electrolytic UO₂ - Comparison of 0.222" Step with 0.156"
 Step in Production of -4 +10 Mesh Particles

FIGURE 61
Effect of Pressure on Production of Intermediate Fraction UO_2 Particles

FIGURE 62
Preparation of UO₂ Feed for Vibratory Compaction by Parallel Plate Crushing

the product from the parallel plate crushing operation, and blending the three size fractions was attempted. A Model 30 Red Devil Paint Conditioner* with a figure eight oscillatory motion was modified to allow variable speed. The electrolytic UO_2 was placed in a heavy-walled 3-in.-diam by 4-in.-long steel can containing steel or alumina balls and shaken at high speed. The impact of the balls shatters the large pieces of UO_2 and further size reduction by impact and grinding occurs. The results are shown in Table XIX. The amount of -100 mesh material formed is relatively independent of initial particle size and is a strong function of container and batch size, and apparently the process of pulverization to minus 200 mesh fines does not go to completion in shaking times of 1 to 2 hr. Reducing the shaking speed from 1315 shakes/min to 940 shakes/min produces a sharp decrease in the rate of shattering of the largest particles, and even a much longer operating time does not carry the process to completion. Comparison of Runs SH-7 and PS-5 shows that using alumina balls, which are much lighter than the steel balls, has little effect on the process of size reduction. Shaker speed has the most significant effect on the process of size reduction. Doubling the speed of the shaker has a dramatic effect on the rate of fines production, producing 94% -200 mesh fines in 30 min. Further size reduction work with this equipment was delayed indefinitely until a higher speed system could be devised.

To demonstrate the second phase of its multipurpose capabilities, the paint conditioner was used to screen UO_2 on three 3-in.-diam sieves. As shown in Table XX, 200 shakes/min appeared to be an optimum speed for sieving. In Run SH-1 100 shakes/min was inadequate to pass the UO_2 through the 10 mesh screen, while 400 shakes/min degraded some of the +10 mesh particles. Confirmation that 200 shakes/min did not degrade the particles appreciably is found in the comparison with the screen fractions obtained by a standard screen analysis of the feed. Reducing the shaking time from 15 min to 10 min produces no significant change in the screen fractions, indicating that sieving was complete at 10 min and that particle degradation had not occurred at 15 min.

*Red Devil Tools, Union, New Jersey

TABLE XIX

FINES PRODUCTION BY HIGH-SPEED IMPACTION

Equipment: Model No. 30 Red Devil Paint Conditioner modified for variable speed. Heavy walled
3 in. diam x 4 in. length cylindrical steel can with (3 to 6) 3/4 in. diam steel balls.

Run No.	Speed, Shakes/min	Shaking Time, min	Feed Material	Product Size Distribution, percent				Comments
				+100 mesh	-100 +200	-200 fines		
PS-2	1315	30	-3/4 in. +1/2 in. HS-5 deposit	48.5	19.1	32.3		
PS-3	1315	60	-3/4 in. +1/2 in. HS-6	35.0	24.8	40.2		
PS-8	940	345	-3/4 in. +1/2 in. HS-7	26.4	22.7	50.9		
PS-7	940	345	-3/4 in. +1/2 in. HS-7	22.0	16.3	61.7	+3 mesh = 18.1%	
PS-4	1315	30	-10 + 35 mesh HS-6	38.4	25.7	35.8	(small can, 1/6 batch size)	
PS-5	1315	30	-10 + 35 HS-6	51.8	18.2	29.8		
PS-6	1315	100	-10 + 35 HS-6	30.2	22.4	47.3		
				<u>-10+35</u>	<u>-35+65</u>	<u>-65+200</u>		
SH-7	1315	27	-10 + 35 HS-7	35.1	23.5	15.9	38.3	3/4 in. Alumina balls
SH-8	2420	30	-10 + 35 HS-7	0.4	0.07	4.8	94.1	Alumina balls

137

BWW-354

TABLE XX

SIEVING STUDIES IN MULTIPURPOSE EQUIPMENT

Equipment: Model No. 30 Red Devil Paint Conditioner modified for variable speed.
3 in. diam X 5/8 in. depth sieves - Batch Size 500-1000 grams UO₂.

<u>Run No.</u>	<u>Time,</u> <u>min</u>	<u>Speed,</u> <u>shakes/min</u>	<u>+10 mesh</u>	<u>-10 +35</u>	<u>-35 +65</u>	<u>-65 fines</u>
----------------	----------------------------	------------------------------------	-----------------	----------------	----------------	------------------

Feed Material: HS-5 Deposit, from Iler Disc Pulverizer Crusher
Run, uncharacterized, same feed for each run.

SH-1	15	100	83.1	5.8	5.2	5.8
SH-2	15	200	21.2	15.7	13.4	46.2
SH-3	15	400	7.8	14.5	14.0	63.7

138

Feed Material characterized by Run SH-4

SH-4	15	Standard Shaker	63.4	12.5	4.4	19.6
SH-5	15	200	59.7	13.6	7.1	19.6
SH-6	10	200	58.8	13.9	8.1	19.0

BNWL-354

Blending operations were not conducted with the paint conditioner, although the experiments with pulverizing and screen had encouraged the concept of using the paint shaker as a multipurpose device.

Ball Milling

The results of a series of ball milling tests conducted with electrolytic UO_2 are shown in Figure 63. A two quart jar containing alumina pellets and the unwanted -10 + 35 mesh size fraction was rotated at 60 rpm for various time intervals. The results show that about 8 hr are required to grind 99% of the material to -100 mesh and 11.7 hr are required to produce 99% -200 mesh fines. The initial curvature in the size fraction versus time curve is due to the time lag produced in getting the +35 mesh particles ground down to the largest screen size (100 mesh).

A remotely operable ball milling apparatus with a stainless steel jar was constructed. Since previous experience had indicated that some iron would be introduced into the product the ball mill jar was lined with Unichrome[®], and tests were conducted to determine the amount of organic material that appeared in the UO_2 product.

Ball milling of an electrolytic UO_2 feed material initially containing 38 ppm chloride for 19 hr produced a product containing 245 ppm chloride, which corresponds to 365 ppm polyvinyl chloride, the principal ingredient of Unichrome. Ball milling for a total of 97 hr produced 350 ppm chloride or 575 ppm polyvinyl chloride. Spectrometric analysis also showed the presence of several hundred ppm of oil which may have corresponded to the plasticizer in the Unichrome. This Unichrome contamination of the fines product in the Salt Cycle demonstration⁽⁷⁾ forced a return to all steel ball mills after the first recycle fuel element had been fabricated.

OFF-GAS TREATMENT

The conventional packed column caustic scrubber used to remove chlorine and hydrogen chloride from the off-gas in the pilot plant operations is described in the equipment section of this report (page 47).

[®] E. I. du Pont de Nemours and Company

FIGURE 63
Ball Milling of Electrolytic UO_2

Caustic Scrubber for the Salt Cycle Demonstration

The caustic scrubber for the Salt Cycle demonstration consisted of a 60 gallon reservoir surmounted by a 6-ft-high, 7-in.-diam tower packed with 5 ft of 3/4-in. polyethylene Raschig rings and fitted at the top with a 6-in. nickel mesh for de-entrainment. The scrubber and other auxiliary equipment such as filters and pumps are described in the report of the Salt Cycle demonstration.⁽⁷⁾ The caustic in the system reached 60 °C at times because of the neutralization reaction. The reservoir was first made of Hastelloy C, but corrosion in the vapor space at the flange made it necessary to replace the inlet into the gas space by a submerged Teflon[®] inlet line. A water line had to be installed in the off-gas line to flush out the caustic that plugged the submerged inlet line periodically. Corrosion of the Hastelloy C in the vapor space eventually caused a leak and the reservoir was replaced by a polyvinyl chloride tank that held up well under the combined peroxide, caustic, hypochlorite, chlorine, and hydrogen chloride atmosphere.

Hypochlorite Destruction

Chlorine reacts with caustic to produce hypochlorite in the following reaction.

The auxiliary tanks in which spent caustic was stored in the Salt Cycle demonstration were made of stainless steel, which is corroded by hypochlorite. Therefore, the hypochlorite had to be destroyed before it left the caustic scrubber. The 15 wt% NaOH solution was first treated with ammonia and later urea to destroy the hypochlorite by the following reactions:

The hydrolysis of urea in the NaOH solution resulted in the ultimate formation of a sub-micron mist of NH_4Cl which plugged the tower off-gas lines, leading to the abandonment of the second method. Similar behavior was obtained with ammonia.

[®] E. I. du Pont de Nemours and Company.

The reaction of hydrogen peroxide with hypochlorite:

achieved complete destruction of the hypochlorite without adverse side effects. A 10% excess of 15 wt% H_2O_2 was added at hourly intervals. The evolution of oxygen was not a serious problem at this addition rate, although appreciable foaming occurred when a large batch of peroxide was added to a caustic solution containing a high concentration of hypochlorite. The addition of the 15 wt% H_2O_2 increased the volume in the recirculating tank at a rate of 1.25 liters/hr. An estimate of the evaporation rate from the tank indicates a loss at the rate of 0.75 liters/hr. This resulted in a volume increase of 9 gal during a dissolution run, while at least 12 gal freeboard existed in the scrubber.

Chlorine Recovery by Liquefaction

Because of the large volumes of waste caustic-chloride solutions produced by the scrubber, a study of the recovery of chlorine from the off-gas by liquefaction was made in the pilot plant. The details of this study and of the removal of radioiodine from the off-gas by liquefied chlorine are reported separately.⁽³⁶⁾ The tests showed that liquefaction of chlorine at -100°C from the off-gas could recover nearly all the chlorine if noncondensable gas inleakage to the salt pot is minimized, could reduce scrubber caustic requirements by a factor of ten, and could produce high iodine decontamination factors by the formation of iodine trichloride in the cold trap.

ACKNOWLEDGMENTS

This work was performed under the guidance of A. M. Platt and later W. H. Swift, Managers, Chemical Engineering Development Operation, Hanford Laboratories, General Electric Company. During the progress of the work, this unit was transferred to Battelle-Northwest and became the Engineering Development Unit, Chemical Development Section, Chemistry Department.

The success of the experimental work in this program was largely due to the efforts of engineering technicians D. H. Walker, J. R. Nance, R. C. Niemuth, and D. H. Siemens, who assisted in the design and operation of experiments and in interpretation of the results.

Our thanks also go to the rotational technical graduates, J. R. Morrissey, D. C. Brandt, and G. R. Bloom, who conducted experiments that aided in the process development.

Much unpublished data is quoted here from the work of and from discussions with G. E. Benedict, J. L. Swanson, R. L. Braun, M. C. Lambert, and W. H. Yunker of the Chemical Separations Unit, Chemical Research Section and W. L. Walker and R. F. Maness of the Materials and Process Chemistry Unit, Chemical Development Section.

The authors are indebted to D. W. Brite, L. P. Murphy, and others of the Ceramics Fuel Development Operation, General Electric Company, whose evaluations of our product are reported elsewhere. (37,38,39,40)

REFERENCES

1. R. W. McKee. Economic Evaluation of Close-Coupled Fuel Processing with Plutonium Recycle, BNWL-28. January, 1965.
2. A. R. Gibson and L. L. Wassell. Extraction of Uranium and Uranium Dioxide from an Australian Ore Concentrate by a Chloride Route, AERE Rept. M/R 2513. 1958.
3. P. W. Smith. Preliminary Cost Estimate for the Electrolytic Conversion of Uranium Oxide to Reactor Grade Uranium Dioxide, HW-73333. April 11, 1962.
4. W. R. Bond. A Preliminary Economic Study of the Preparation of Reactor Grade PuO_2-UO_2 by the Salt Cycle Process, HW-83984. September 9, 1964.
5. G. E. Benedict and R. A. Nixon. Hanford Salt Cycle Process I. Plutonium Chemistry, HW-SA-3622. General Electric Company, Richland, Washington. July 17, 1964.
6. G. E. Benedict, L. G. Morgan, and R. A. Nixon. Plutonium Chemistry of the Salt Cycle Process, in preparation December, 1966. Pacific Northwest Laboratory, Richland, Washington.
7. W. R. Bond, G. Jansen, Jr., and L. K. Mudge. Demonstration of the Salt Cycle Process in a High Level Radiochemical Facility, BNWL-355. December, 1966.
8. J. E. Bodine, J. Guon and R. J. Sullivan. Second-Cycle Airox Reprocessing and Pellet Refabricating of Highly Irradiated Uranium Dioxide, NAA-SR-11375. August 31, 1965.
9. J. L. Swanson, G. E. Benedict, R. C. Smith and G. R. Horn. Demonstration of an Irradiated UO_2 Fuel Cycle: First Recycle, HW-69027. September, 1961.
10. E. M. Vander Wall, H. T. Hahn, and D. L. Bauer. Salt-Phase Chlorination of Reactor Fuels II. ARCO Process Definition and Scoping Studies, IDO-14525. October 28, 1960.
11. J. J. Reilly. Status Report, Reprocessing of Reactor Fuels by Volatilization Through the Use of Inert Fluidized Beds, BNL-663. May, 1961. (Classified) (See Reference 12)
12. "Research and Development on Nonaqueous Processing," Reactor Fuel Processing Quarterly, vol 4, no. 4, pp 33-34. Argonne National Laboratory. October, 1961.
13. "Research and Development on Fuel Processing," Reactor Fuel Processing Quarterly, vol 3 no. 4, p 34. Argonne National Laboratory. October, 1960.
14. W. R. Bond, G. Jansen, Jr., and L. K. Mudge. Hanford Salt Cycle Process II. Engineering Development in a High Level Radiochemical Facility, HW-SA-3527, General Electric Company, Richland, Washington. August 17, 1964.
15. E. M. Levin, C. R. Robbins and H. F. McMurdie. Phase Diagrams for Ceramists, The American Ceramic Society, Inc., 1964.
16. R. L. Braun. Unpublished data. General Electric Company, Richland, Washington. 1962. Personal communication.

REFERENCES Continued

17. L. K. Mudge. Unpublished data. General Electric Company, Richland, Washington. 1962.
18. R. K. Willardson, J. W. Moody and H. L. Goering. The Electrical Properties of Uranium Oxides, BMI-1135. September 25, 1956.
19. J. L. Bates, C. A. Hinman, and T. Kawada. Electrical Conductivity of UO_2 : Part I. Single Crystals, BNWL-296 Pt I. August, 1966.
20. H. J. Anderson and R. J. Anicetti. Specifications for High Density Uranium Dioxide (Nuclear Grade), HW-74204 REV I. September 9, 1963.
21. H. J. Anderson. Specifications for Nuclear Grade Mixed Oxides (UO_2 - PuO_2), Hanford Salt Cycle Compactible Powder, HW-84512-RD. November 16, 1964.
22. C. E. Huck and O. H. Koski. Development of Salt Cycle Process Instrumentation, HW-74968. September 19, 1962.
23. G. R. Bloom. Detection and Oxidation Rate Studies of U(IV) in the Hanford Salt Cycle Process, BNWL-CC-373. Pacific Northwest Laboratory, Richland, Washington. April 26, 1966.
24. G. E. Benedict, K. M. Harmon, G. Jansen, Jr., L. K. Mudge, and F. A. Scott. Production of Reactor Fuel Oxides from Molten Chloride Salt Solutions, HW-SA-2915. General Electric Company, Richland, Washington. May 20, 1963.
25. J. J. Cadwell. Quarterly Progress Report for January, February, March 1962, Fuel Development Operation, HW-72347. General Electric Company, Richland, Washington. April 16, 1962. (Classified)
26. R. F. Maness. Unpublished data. General Electric Company, Richland, Washington. 1962. Personal communication.
27. W. H. Yunker. "Chloride Contamination in Electrolytic UO_2 ," Quarterly Progress Report, Research and Development Programs, Executed for the Division of Reactor Development, July, August, September 1963, HW-79280. General Electric Company, Richland, Washington. October 1963.
28. G. E. Benedict, W. R. Bond, G. Jansen, Jr., L. G. Morgan, and J. R. Lundquist. Status of the Salt Cycle Process for Processing Oxide Fuels, BNWL-SA-205. Pacific Northwest Laboratory, Richland, Washington. September 3, 1965.
29. G. R. Bloom. Melt Atmosphere Control Studies for the Hanford Salt Cycle Process, BNWL-CC-372. Pacific Northwest Laboratory, Richland, Washington. April 26, 1966.
30. Unpublished data. Chemical Separations Operation, General Electric Company, Richland, Washington. 1961.
31. P. D. Miller, E. L. White, D. C. Drennen, C. H. Lund, H. J. Wagner, A. M. Hall and W. K. Boyd. Development of Container Materials for the Fused Chloride-Electrolytic Fuel-Recovery Process, BMI-1539. August 28, 1961.
32. W. L. Walker. Unpublished data. General Electric Company, Richland, Washington. 1962. Laboratory notebook.

REFERENCES Continued

33. J. H. Kleinpeter. Non-Metallic Material Studies for Molten Salt Processes, HW-72369. January 22, 1962.
34. J. E. Morrissey. Preliminary Study on the Application of a Frozen Wall and Electrolytic Heating to Molten Salt Baths, HW-72572. February 2, 1962.
35. D. C. Brandt. Alternating Current Heating of Molten Salts, HW-75468. November 28, 1962.
36. L. K. Mudge and J. R. Lundquist. Chlorine Recovery and Radioiodine Behavior in the Salt Cycle Process, BNWL-279. July, 1966.
37. J. J. Cadwell. Quarterly Progress Report for July, August, September 1960, Fuel Development Operation, HW-69085. General Electric Company, Richland, Washington. October 15, 1960. (Classified)
38. J. J. Cadwell. Quarterly Progress Report for April, May, June 1961, Fuel Development Operation, HW-70557. General Electric Company, Richland, Washington. July 15, 1961. (Classified)
39. J. J. Cadwell. Quarterly Progress Report for July, August, September 1961, Fuel Development Operation, HW-71422. General Electric Company, Richland, Washington. October 13, 1961. (Classified)
40. J. J. Cadwell. Quarterly Progress Report for April, May, June 1962, Fuel Development Operation, HW-74377. General Electric Company, Richland, Washington. July 20, 1962. (Classified)

ONSITE DISTRIBUTIONCopy NumberPacific Northwest Laboratory

1	J. M. Atwood
2	G. E. Benedict
3	A. G. Blasewitz
4	W. R. Bond
5	R. E. Burns
6	C. R. Cooley
7	D. R. deHalas
8	W. L. Delvin
9	K. Drumheller
10	W. L. Hampson
11	K. M. Harmon
12 - 31	G. Jansen, Jr.
32	B. M. Johnson
33	A. M. Platt
34	W. E. Roake
35	R. C. Smith
36	J. L. Swanson
37	E. E. Voiland
38	M. T. Walling
39 - 41	Technical Information Files

Richland Operations Office

42	R. K. Sharp
43	C. L. Robinson

Isochem Inc

44	P. W. Smith
----	-------------

OFFSITE DISTRIBUTION SPECIAL

45	W. A. Emel Idaho Nuclear Corporation Idaho Falls, Idaho
46	J. Schmets (CEN) Mol, Belgium
47 - 51	Division of Technical Information Extension