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METALLURGY AND CERAMICS

UNITED STATES ATOMIC ENERGY COMMISSION

EXPANDED SCALE PROCESS DEVELOPMENT OF THE ELECTROLYTIC PRODUCTION OF THORIUM FROM ThCl_4 IN EXTERNALLY HEATED ELECTROLYTIC CELLS.

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SUMMARY

The scale-up of an electrolytic process for the production of thorium metal developed by Horizons Incorporated has been successfully carried out and the commercial feasibility of semi-continuous operation of this process has been demonstrated.

An electrolytic cell capable of producing approximately seven pounds of thorium metal per hour of electrolysis was adopted to a removal chamber system which made possible semi-continuous cell operation under controlled inert atmosphere conditions. Good quality thorium metal was produced, with as-cast hardness as low as Brinell 50 and HCl-insolubles content of melted thorium buttons as low as 0.57 per cent.

A cathode cooling system was developed and proved to be an effective means of preventing cathode deposit loss. A campaign current efficiency of 72.8 per cent was achieved, with deposit loss in the cell being essentially nil. The process yield was 86 per cent.

The major materials of construction, nickel and graphite, were observed to possess very satisfactory service life.

In general, the equipment modifications and operational concepts tested during two extended electrolytic campaigns proved to be satisfactory for use on a proposed commercial prototype cell. However, the need for further system modifications to bring about more efficient and economical operation became apparent during these campaigns. Major emphasis must be placed on suitable modifications to minimize process loss of thorium values.

CONCLUSIONS

Based on the results obtained in the two electrolytic campaigns described in this report, it can be concluded that the electrolytic process for the production of thorium metal is a commercially feasible process.

The process has been successfully expanded to a pilot plant sized cell capable of producing 25 to 30 pounds of thorium metal per electrolytic run, at a production rate of approximately seven pounds of thorium per hour of electrolysis.

The basic design of a removal chamber system, which permits semi-continuous operation of the electrolytic cell under controlled inert atmosphere conditions, has been shown to be satisfactory. Thorium metal of good quality has been produced in the pilot plant cell as a result of the relatively inert cell and removal chamber system atmosphere.

The problem of cathode deposit loss or partial deposit loss has been overcome through the development of a cooled cathode. Greatly improved current efficiencies have resulted from this development.

The major materials of construction, nickel and graphite, have been found to possess very satisfactory service life. It has been tentatively shown that anode shielding directly below the cathode by a non-conductor such as alundum has a beneficial effect on cathode deposit growth, producing cathode deposits of a more desirable shape from the standpoint of deposit temperature control.

A thorium chloride cell feed of at least 45 per cent thorium concentration has been shown to be necessary in order that adequate process control can be maintained during continuous operation of the electrolytic cell.

Operation at constant DC current conditions has been found desirable, and the utility of DC voltage readings as a means of electrolytic process control has been demonstrated.

A positive cell system pressure must be maintained at all times to minimize back-diffusion of air into the system.

To make the operation more efficient and to reduce the manpower requirement still further, additional modifications of the mechanical handling system must be made.

The charging system must be revised both from the standpoint of increased process efficiency as well as to prevent loss of thorium values by splashing of the electrolyte onto cell components.

Provisions must be made for efficient recovery of thorium values from dust and volatilized thorium chloride condensate deposition on cell and auxiliary components.

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INTRODUCTION

Under the auspices of the U. S. Atomic Energy Commission Contract No. AT(30-1)-1335, work has been carried out at Horizons Incorporated in the general field of thorium chemistry and metallurgy. This report is a summary report of one phase of the research and development program, namely, the expanded scale process development of the electrolytic production of thorium from ThCl_4 in externally heated electrolytic cells.

A previous report⁽¹⁾ on the extractive metallurgy of thorium by the electrolysis of fused salts has discussed historical and theoretical aspects of this process and has presented operational procedures, operational variables affecting the production of thorium metal by the electrolysis of the tetrachloride of thorium, and the application of this process in producing high quality thorium metal powder. The report has also described the production of thorium metal both in a laboratory unit capable of producing 200 g. of thorium per run and in an intermediate-sized cell capable of producing four pounds of thorium metal per run. Both of these units were operated on a batch-wise basis.

This report describes the production of thorium metal by a semi-continuous process in an electrolytic cell capable of producing 25 to 30 pounds of thorium per electrolytic cycle.

The cell per se was designed and built at Horizons Incorporated under ONR Contract No. Nonr-394(01). Initial attempts at scaling up the thorium production process in this cell met with major difficulties, chief among these being control of the cell atmosphere and consequent poor quality of metal,

(1) "Investigations for the Production of Thorium Metal" by B. C. Raynes, J. C. Bleiweiss, M. E. Sibert and M. A. Steinberg, Horizons Incorporated, November, 1954.

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control of cathode temperature and resultant loss of portions of the cathode deposit, and crucible leakage. The last named problem was overcome by the substitution of a Graph-i-tite (carbon-impregnated graphite) crucible for the graphite crucible previously used.

To overcome the cathode temperature control problem, a cathode design involving a cooling system was initiated, and a removal chamber system was developed to make possible semi-continuous operation of the cell under controlled inert-atmosphere conditions. Adaptation of a revolving removal chamber system to an existing cell not intended for this type of continuous operation proved to have several disadvantages. For example, the cell layout made it mandatory to charge make-up salt through the removal chamber system rather than to the cell directly.

The purpose of the campaigns described in this report was twofold. The first, and minor, purpose was to scale up the process for the production of thorium by fused salt electrolysis to a pilot plant scale. The second, and major, aim of the campaigns was to check out the operation of several equipment modifications and revised operational concepts which were intended for use on a subsequent commercial prototype cell. The latter cell, now under construction, is of somewhat different design from the Mark VI electrolytic cell used for this phase of the development program.

The process for the electrolytic production of thorium metal can be summarized as being the electrolysis of fused thorium tetrachloride in a molten sodium chloride - potassium chloride bath under an argon atmosphere. The thorium is deposited as dendritic crystalline metal in a matrix of salts from

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which it can be readily separated by water leaching. The thorium metal is further purified by an acid treatment.

The overall electrolytic cell reaction is

The normal electrolytic cycle in semi-continuous operation entails charge make-up addition, a charge melting period, a cathode pre-heating and polarizing period, the electrolysis, cathode cooling in one of a pair of removal chambers, and cathode deposit chipping. A second electrolytic cycle is carried out while the first cathode is cooling and made ready for a third cycle.

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PROCESS DESCRIPTION

1. EQUIPMENT REQUIREMENTS FOR ELECTROLYTIC OPERATIONS

The Mark VI electrolytic cell used in the described campaigns has a capacity for producing approximately 25 to 30 pounds of thorium per run. Design of this cell is based on smaller scale electrolytic cells used at Horizons Incorporated. At this stage of the process development the Mark VI cell is not intended as a prototype of a commercial cell. Operation of this unit has been carried out at levels as high as 2,500 amperes. Very briefly described, the unit consists of a nickel-clad mild steel shell which is completely water-jacketed. It is insulated with refractory insulating brick on its sides and bottom. A sectioned graphite heating element is located in the annular space between the insulating brick and a Graph-i-tite crucible. The crucible serves as both anode and crucible and can accommodate approximately a 375 pound charge of molten salts. An 18 inch diameter nickel slide valve located between the cell and a removal chamber assembly is closed off to allow cell evacuation to 300 μ or less prior to a campaign. With a new crucible, evacuation is carried out at 800°C. Subsequent evacuations are carried out at 200°C. Electrolytic operations are then carried out under an argon atmosphere. The chlorine take-off line is provided with a liquid seal which permits operation at a positive pressure of approximately two inches water gauge.

The removal chamber assembly consists of a water-jacketed stationary circular plate flanged to the top of the nickel slide valve and another circular

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plate which is free to rotate. Neoprene "O" rings provide the seal between the two plates during electrolysis. During rotation positive pressure is maintained in the system by means of a liquid seal at the plate periphery. The rotating plate has openings leading to two removal chambers which can be positioned over the slide valve. An inert-atmosphere charge hopper can be attached to the rotating plate at a third opening and batchwise charging through a double valve system can be carried out between electrolyses. Sampling of the bath is also accomplished through the charge opening.

The removal chambers are nickel-clad cylinders approximately 48 inches high. They are water-jacketed and have provisions for evacuation and argon flushing. The cathode passes through a rubber boot seal at the top of the chamber and extends into the crucible to the desired level. The cathode has a 12 inch by 3-1/2 inch diameter tip of Hastelloy "C" pipe filled with copper except for a cooling cavity. The cathode shaft is made of nickel. The major portion of the shaft is water-jacketed, while the portion of the shaft immediately above the tip is not water-cooled but protected by a graphite sleeve. An air line passes through the hollow shaft core and carries cooling air to the cathode tip cavity.

Major pieces of auxiliary equipment include a saturable core reactor as an AC power source for heating, selenium rectifiers and a constant current regulator, a scrubber for neutralizing the chlorine given off during electrolysis, a source of compressed air, and a dust collecting system. A vacuum pump, argon manifold, manometer, temperature and voltage recorders and other instrumentation complete the list of major items.

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2. OPERATION OF THE MARK VI ELECTROLYTIC CELL

A detailed description of cell operation is given on page 34 of this report.

Raw materials used for electrolysis are thorium chloride-sodium chloride-potassium chloride cell feed and sodium chloride for diluting the cell feed to the desired thorium concentration. The sodium chloride make-up is used without pre-drying. The sodium chloride-potassium chloride content of the cell feed is present in eutectic mixture proportions. Both sodium and potassium chlorides can be of commercial grade. The thorium values are derived from mantle-grade thorium tetranitrate supplied by the A. E. C. The thorium chloride cell feed is prepared at this laboratory by a process developed by Horizons Incorporated.

A check is made on bath composition by withdrawing samples of bath after each electrolysis, dissolving a 20-gram sample in 100 ml of water at room temperature, and obtaining a hydrometer reading of the resulting solution. A conversion curve for converting the hydrometer reading to "per cent thorium chloride" is presented as Figure 1. The sampling procedure is subject to considerable error unless a truly representative sample is obtained. Concentration stratification has been found to be quite severe.

3. METAL RECOVERY

Cathode deposits are chipped manually from the cathode. Each deposit is passed through a jaw crusher, and then through a roll crusher.

The crushed deposit is fed slowly into the top of a counter-current

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cone washer through which a stream of water is flowing. The initial wash water, which contains most of the soluble salts, is collected, and the thorium content recovered by precipitation with Na_2CO_3 . Fresh tap water is used for a period of fifteen minutes, after which time the wash water is recycled for a period of ninety minutes.

The metal is then acid-treated with a 5% (volumetric) solution of sulphuric acid for a period of thirty minutes. The metal is then washed free of sulphuric acid by means of tap water, the washing being continued until the pH of the effluent water is identical to that of the incoming wash water.

The metal is withdrawn from the cone washer, filtered by suction and dried on the suction filter, using acetone to hasten the removal of water. It is then dried in an oven at a temperature of $45^\circ\text{C}.$, after which it is packaged under argon.

Particle size is determined by screen-testing a 1,000 g. representative sample. HCl-insolubles are determined on a representative sample of the metal powder, and a compressed 15 g. portion of the metal is vacuum melted to form a button, which is subsequently tested for Rockwell hardness and for HCl-insolubles.

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DISCUSSION OF ELECTROLYTIC OPERATIONS, MARK VI-87-8 CAMPAIGN

The prime purpose of this campaign was to serve as a shake-down run for several cell design modifications intended for use on a subsequent commercial prototype electrolytic cell and to prove out various concepts of cell operation.

1. CAMPAIGN SUMMARY

The Mark VI electrolytic cell campaign Mark VI-87-8 was a semi-continuous operation of 78 hours duration. Fourteen cathode deposits were removed from the cell during the campaign. The major purpose of the campaign was the evaluation of certain modifications of process equipment and changes in process operation aimed at making the electrolytic process a continuous process. In principle the equipment and operational modifications proved to be satisfactory; however, the need for several further modifications was brought out during the campaign.

Table I presents a very brief summary of thorium metal production and operational data of the campaign.

Table I

Statistics on First Continuous Mark VI Electrolytic Campaign

Total weight of thorium charged to cell	442	lbs.
Total weight of deposits recovered (metal and salt)	532	lbs.
* Total weight of thorium metal recovered	261.5	lbs.
Least, average, and largest deposits (metal and salt)	22	lbs.
	38.1	lbs.
	57	lbs.
Least, average, and largest thorium metal deposits	5.9	lbs.
	15.6	lbs.
	31.2	lbs.
Least, average and highest current efficiencies	21	%
	44.5	%
	79	%

Table I (continued)

Least, average, and highest per cent metal in deposits	27 %
	41.2%
	55 %
Total time for electrolytic campaign	78 hours
Total number of cathodes produced	14
Average electrolytic cycle	5.5 hours
* Cumulative current efficiency for entire campaign (includes 42.5 lbs. of metal recovered from bottom of cell)	54.2%

* Additional quantities of metal had been converted to thorium carbide in the cell crucible.

Table II presents data concerning individual electrolytic cycles of the Mark VI-87-8 campaign.

Table II.

Approximate Analysis of Individual Electrolyses in Mark VI-87-8 Campaign

Electrolysis No.	Total Amp-hrs.	Total Wt. of Deposit (lbs.)	Per cent Metal in Deposit	Metal Wt. (lbs.)	Current Efficiency
1	6,000	42	30	12.6	44%
2	6,000	22	27	5.9	21%
3	6,000	34	32	10.9	38%
4	8,000	40-1/2	34	13.8	36%
5	8,000	57	44	25.1	67%
6	6,000	26	33	8.6	30%
7	8,700	25	50	12.5	30%
8	10,000	39-1/2	48	19.0	40%
9	6,300	40	32	12.8	43%
10	8,200	56-1/2	55	31.2	79%
11	5,850	31	38	11.9	43%
12	10,000	47	51	23.9	50%
13	7,000	48-1/2	44	21.3	64%
14	5,300	23-1/2	41	9.6	38%

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2. REMOVAL CHAMBER AND CHARGING SYSTEM

This campaign marked the first application of a removal chamber system on a large-scale cell at the laboratories of Horizons Incorporated. The removal chamber system was to allow removal of a cathode deposit from the cell without contamination of the cell atmosphere by air. The use of a two-chamber system was also a step in the direction of the continuous-operation concept.

In principle, the operation proved out both of the aims of the removal chamber system. The system, however, did not provide all the cell atmosphere protection that had been hoped for, due to warpage of the stationary base plate of the assembly which resulted in an imperfect O-ring seal between the stationary and rotating plates, and also prevented proper functioning of the liquid seal in the chlorine take-off line. However, it was felt that modifications to both plates could improve this condition. Even with this imperfect protection, the thorium metal produced in this campaign was of higher quality than thorium metal produced in this cell in previous attempts without a removal chamber system.

In order to insure that no air enters the electrolytic cell, thus allowing contamination of the bath and ultimately of the deposits, a positive seal must be maintained not only around the perimeter of the two removal plates, but also around the removal chambers themselves. This is necessary for several reasons -- namely, to prevent air contamination of the cell atmosphere through a removal chamber which has been opened for deposit removal, to make possible evacuation and subsequent argon flushing of a chamber prior to electrolysis, and to make possible the maintenance of an inert atmosphere

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in the chambers while a deposit is cooling down prior to being chipped off the cathode. After the first run in this series it was found impossible to evacuate the chambers due to the lower plate warpage. It appeared likely that warpage of the plate was due to welding stresses rather than operational thermal stresses, since the plate, made of one-inch thick nickel, is water-jacketed to a large extent. The initial deposits of the series showed evidence of cell atmosphere contamination, i.e., the deposit surface was generally contaminated with yellowish and whitish deposits, these undoubtedly being oxides or nitrides of thorium. In later runs the effect of the poor seal was counteracted by an excessive argon flow into the removal chamber throughout the cooling period.

Warpage of the plate not only permitted contamination of the cell atmosphere through the removal chamber assembly but also made the liquid seal in the chlorine take-off line inoperative. A liquid seal of even one inch depth provided a seal of sufficient magnitude that the chlorine gas produced during electrolysis tended to escape between the stationary and rotating plates rather than going through the liquid seal and out into the scrubber system. The sealing liquid was therefore removed, thus permitting back diffusion of air into the system. A one-way swing valve in the chlorine line was also tried, but excessive dust carryover in the chlorine stream caused frequent sticking of the valve.

The Mark VI-87-8 campaign was the first attempt at continuous operation. In previous campaigns runs were entirely batchwise, the cell being emptied and re-charged prior to the electrodeposition of a second,

third, or succeeding deposition. The only discontinuity in the operation was the turn-around time required for pulling a deposit-laden cathode out of the bath and rotating the removal chamber away from the electrolysis position, charging make-up feed, and rotating the second removal chamber and cathode into the electrolysis position. Turn-around time was as low as 45 minutes and was limited mostly by the time required for melting down the make-up charge. The campaign was semi-continuous for 78 hours, during which time 14 cathode deposits were produced,

Termination of the campaign was brought about by two factors:

(1) The supply of cell feed had been depleted, and (2) the bath level had risen to too high a level. This was due to the use of cell feed of relatively low thorium concentration (approximately 39% Th). In order to maintain the proper thorium content in the bath, excessively large amounts of cell feed were required. While previous smaller scale experiments at the laboratory had shown that the use of a 42% Th cell feed would permit nearly continuous operation at a satisfactory thorium concentration, the experience in this campaign pointed to the need for at least a 45% Th cell feed for satisfactory operation of a large cell.

From a purely mechanical viewpoint, the method of charging from the removal chamber level had the drawback of causing splashing when the make-up charge hit the molten bath. Make-up cell feed additions were charged through a double valve port which was built into the cell removal chamber assembly. The technique involved rotating the removal chamber plate until the charging port was directly over the cell, after which the entire charge of make-up salt was allowed to run directly into the cell through a 3-inch pipe opening.

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The material, weighing from 50 to 100 pounds, had a free-fall drop of approximately six feet before hitting the level of the electrolytic bath, which caused severe splashing. A sizable poundage of salt was found layered above the level of the crucible top, on portions of the heat reflectors, and on insulation in the upper portion of the cell as a result of splashing. It was felt that extending the crucible with a cylindrical sleeve would prevent a future occurrence of at least a portion of this problem. A better solution, of course, would be to charge from a lower level. This, however, is not feasible with the Mark VI cell, since the cell was not originally designed for a removal chamber assembly and has no accessible areas for a charging port on the cell itself when the removal chamber assembly is in position.

3. CATHODE COOLING SYSTEM

Past experience in this and other medium-sized electrolytic cells had generally indicated that cathode cooling was one of the major factors to be considered in a successful electrolytic operation. This series of runs was the first experiment in which water cooling over the length of the cathode was utilized in conjunction with cathode tip cooling by means of air. Air cooling alone had been utilized successfully in a smaller cell at current levels of 1,500 amperes.

The Mark VI cathode, which measures some 12 feet in overall length, is water-cooled on the outside to within approximately 36 inches of the lower tip. This serves a multiple purpose of improving the rate of heat

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extraction from the cathode tip, allowing the use of a rubber packing gland at the top of the removal chamber to prevent air leakage around the cathode, and contributes somewhat to decreasing the overall cell voltage by allowing the cathode to run at a lower temperature, and hence with a slightly lower path resistance for DC electrical circuitry.

In addition to the water cooling on the shaft of the cathode, the actual cathode tip, where the metal deposit is formed, was supplied with internal air cooling in order to extract heat directly at its source.

The Mark VI-87-8 campaign was made during a period of extremely high temperature and humidity. Ordinarily this condition should not have interfered with successful air cooling. However, the air after-cooler coils had become fouled, resulting in excessive moisture content of the air, subsequent condensation of water in the air flowmeter, and consequent inability to achieve adequate airflow into the cathode tip on several of the runs. Unfamiliarity with the operating characteristics of the air cooling system as, for example, starting up the air cooling too late in the run, also resulted in poor cooling efficiency on some of the runs.

Excellent air cooling, as shown by the cathode tip temperature curves, was obtained on only five runs (numbers 1, 5, 9, 10 and 13) out of 14 runs. It is interesting to note that three of these runs (5, 10 and 13) showed high current efficiencies. Number 1, being the first of the series, might be expected to have a somewhat lower current efficiency. Number 9 Run ended up with a bath showing essentially no thorium content and should probably have been terminated 1,000 ampere hours earlier than it was. At that point

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a voltage rise indicative of an end point was reached. These facts offer a partial explanation of the low current efficiency of this run despite excellent cathode cooling.

In the runs where current efficiency was extremely low, air cooling was found to have been ineffective, or almost non-existent in some cases, due to difficulties in the cooling system. The run with the lowest current efficiency of the series also was the run having the worst cathode tip temperature control, the lowest cathode temperature in the run being 710°C. A contributing factor to the low current efficiency of 21 per cent was the fact that no make-up salt was added prior to the run.

In general it was found that little or no metal loss from the cathode deposit occurred in runs where satisfactory current efficiencies were obtained. Effective cathode cooling has been found to be a major factor in preventing loss of deposit and therefore in the success or failure of an electrolysis. Cooling can be effective, however, only through a deposit thickness of approximately 2-1/2 inches. Beyond that range it has not been found possible to provide sufficient heat extraction by means of internal air cooling.

4. POWER SOURCES AND CONTROLS

This campaign marked the first use of a constant current control unit on the DC power supply for the Mark VI electrolytic cell. It operated satisfactorily throughout the campaign, and generally within the specifications provided by the manufacturer, i.e., within an accuracy range of 10 per cent.

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Slight adjustments were made periodically during the run to hold the amperage at the exact desired figure, but in general little attention had to be paid to the DC aspect of the program as a result of using the constant current controller.

DC voltage readings provide a source of process control, inasmuch as a voltage rise during electrolysis may be indicative of either bath depletion, localized depletion, or the loss of a portion of the deposit. Unfortunately a recording voltmeter was not available to the project at the time of the campaign.

No direct readings of bath temperature were taken during this campaign, since the crucible and cell design of the Mark VI electrolytic cell makes it impossible to replace burned-out thermocouples during a run. Process control was therefore carried out based on external crucible wall temperatures. This is only an approximation of actual bath temperature and does not reflect thermal changes during the run within the bath itself. Thermocouples placed within the crucible wall, which reflect actual bath conditions to a greater extent, burned out early in the campaign, but could not be replaced due to the cell and crucible design.

5. CELL FEED REQUIREMENTS

Cell feed make-up composition is important from the standpoint of bath temperature control as well as cathode deposit strength. The presence of potassium chloride in the electrolyte lowers the required operating temperature and reduces both thorium loss through volatilization and

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power consumption. Too high a potassium chloride content, however, produces a deposit perimeter of extremely weak, dendritic, and friable structure that is easily lost into the bath. Electrolytes containing higher percentages of sodium chloride do not appear to be as susceptible to the formation of this type of deposit.

For reasons of operating ease and efficiency, the cell feed is produced with potassium chloride and sodium chloride in a 1:1 molar ratio. This ratio has been found to be too high in potassium chloride for satisfactory electrolytic cell operation. When the initial charge melt-down is made, the ratio can easily be adjusted to a ratio which has been found more desirable for producing a strong cathode deposit, i.e., a sodium chloride to potassium chloride ratio of 2:1 by weight. To make such adjustments on subsequent make-up charges poses the problem of excessive dilution of the bath and consequent rise in bath level if proper concentration is to be maintained. This is one of the factors affecting the thorium concentration required in cell feed. Other factors are the per cent metal dragged out in the deposit, the thorium content of the bath salt being dragged out, the actual composition of the electrolyte, and volatilization and mechanical entrainment losses of thorium values from the electrolyte.

For this campaign in the Mark VI cell a feed ranging from 39.4 per cent to 44 per cent thorium, with 1:1 molar ratio sodium chloride to potassium chloride, was utilized as the make-up charges. Additional quantities of sodium chloride were added in order to counteract the salt ratio, though there was a definite limitation to the amount of total salt which could be added due to the size limitation of the crucible. As a result, the sodium chloride

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to potassium chloride ratio dropped from an initial value of 2.53: 1 to a final value of 1.60: 1. At the same time, the bath level increased from an initial depth of 31 inches to almost 36 inches.

Table III presents a hypothetical calculation, using a 70 per cent current efficiency factor and assuming 40 per cent metal content in the cathode deposit, illustrating the thorium concentration requirement in cell feed (not make-up charge) with a 1: 1 molar potassium chloride-sodium chloride base. A run duration of 6,000 ampere hours has been assumed.

Table III

Hypothetical Calculations of Th Concentration Requirement in Cell Feed
(Volatilization Losses of Th Values Neglected)

Initial NaCl: KCl Wt. Ratio	Removed from Bath					Cell Feed		NaCl Make-up lbs.	NaCl: KCl Wt. Ratio in Make-up Charge
	Th as metal lbs.	Th as salt lbs.	Cl ₂ lbs.	Salt lbs.	Th to replace lbs.	% Th	lbs.		
2: 1	20	3.2	12.2	30	23.2	44	52.8	9.2	1.90: 1
2: 1	20	3.2	12.2	30	23.2	45	51.5	10.5	2.16: 1

The data presented in Table III show that the thorium concentration in cell feed must be in excess of 44 per cent if a sodium chloride to potassium chloride weight ratio of 2: 1 is to be maintained in the electrolyte, and if the bath level is to remain constant. When it is considered that thorium value volatilization losses up to 5 per cent (i.e., 5 per cent of thorium values removed as metal plus salt) may occur, the thorium concentration

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requirement is raised by a slight amount, as shown in Table IV below. Thorium chloride is volatilized out of the cell and deposited on the walls of the upper structure of the cell and auxiliary components. Additional quantities are carried out mechanically, entrained in the chlorine gas stream.

Table IV

Hypothetical Calculations of Th Concentration Requirement in Cell Feed
(5% Th Volatilization Loss Assumed)

Initial NaCl: KCl Wt. Ratio	Th as metal lbs.	Th as salt lbs.	Th volatil'n loss-lbs. ThCl ₄	Cl ₂ lbs.	Salt lbs.	Th to replace lbs.	Cell Feed				NaCl: KCl Wt. Ratio in Make-up
							Make- up Th lbs.	NaCl Make-up lbs.			
2:1	20	3.2	1.9	12.2	30	24.4	44 55.5	8.6			1.78:1
2:1	20	3.2	1.9	12.2	30	24.4	45 54.2	9.9			2.01:1
2:1	20	3.2	1.9	12.2	30	24.4	46 53.0	11.1			2.25:1

It becomes apparent, then, that cell feed of at least 45 per cent thorium concentration is required in order that adequate process control can be maintained during continuous operation of an electrolytic cell.

6. MANPOWER REQUIREMENTS

The Mark VI-87-8 campaign was operated with five men on each shift. As familiarity with the various details of the operation was obtained, it became apparent that a four-man crew could handle the physical operations involved with ease and still maintain approximately a 45-minute turn-around time between electrolyses. Improvement of some of the mechanical handling operations could reduce the personnel requirements still further.

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INDIVIDUAL ELECTROLYTIC RUNS, MARK VI-87-8 CAMPAIGN

Prior to the start of the electrolytic campaign the Mark VI electrolytic cell underwent a series of hot evacuations to eliminate residual moisture. The cell was evacuated for two 24-hour periods at 400° F, and in a third evacuation it was brought to 1500° F over a period of twelve hours. After this final evacuation the cell was leak tested, with the nickel slide valve closed. A leak rate of four to five microns per minute was found.

Heat-up for the electrolytic campaign started at 0800 on June 6, 1955. The cell reached operating temperature after 7-1/2 hours, and the first charge was dropped to the cell one-half hour later. Over a period of five hours the entire charge of 377 pounds was charged and melted. This initial charge was composed as follows:

136 pounds Cell Feed 361 - 31 @ 25% Th
90 pounds Cell Feed 361 - 4 @ 25% Th
145 pounds Sodium Chloride
6 pounds Potassium Chloride

The charge contained 57 pounds of thorium, in the form of 92 pounds thorium chloride. Total sodium chloride content was 206 pounds, and total potassium chloride was 83 pounds. The thorium concentration of the initial charge was 15 percent and the ratio of sodium chloride to potassium chloride content was 2.5 to 1. Density of the molten charge was approximately 0.067 lbs./cu. inch. The initial bath depth was 31 inches, and the crucible

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wall temperature used as electrolysis control temperature was 780°C. Argon flow to the cell was maintained at 1.5 L/min., and argon flow to the removal chamber (electrolysis position) was 3 CFH.

Electrolysis Number I.

The cathode was lowered into the cell and preheated to 325°C. After a fifteen minute pre-heat period the DC current was started at polarizing level of 300 A and 5.5 volts. Erratic cathode temperature readings indicated a faulty thermocouple, and the cathode thermocouple was replaced. When the DC was raised to 2000 amps, it was noted that the cathode heat shields were shorting out through the slide valve assembly. This condition was corrected by placing the cathode support clamp on the cathode, and electrolysis was begun at 0010 hours on June 7, 1955. Initial DC during electrolysis was 2000 A at 11.5 V. Two separate chlorine leaks were noted between the stationary and rotating plates of the removal chamber assembly at the start of electrolysis, and the leaks increased in intensity throughout the run. The electrolysis proceeded for 5800 amp-hours, at 2000 amps. Average crucible wall temperature during electrolysis was 725°C. Cathode cooling was adequate throughout the run. Polarizing time at the conclusion of electrolysis was determined by the length of time required for removing the main DC cables from the cathode clamp. In general, this operation required from two to three minutes. The cathode and deposit were hoisted into the removal chamber, with argon flow to this chamber continuing at 3 CFH. The slide valve was closed, and the turntable rotated to the charging position. Following withdrawal of a bath

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sample, the cell was recharged with fifty pounds of Cell Feed 378-1 (containing 44% Th) and six pounds of NaCl. The deposit resulting from the first electrolysis weighed 42 pounds. It was 17" long and approximately 8" in diameter and appeared to be fairly well intact. Several small chunks appeared to have dropped off the deposit.

Electrolysis Number II.

Two and one-half hours after withdrawal of the first deposit, the second cathode was lowered into the cell. Bath depth was 30 inches, and polarization was carried out for 19 minutes at 400 A and 5.0 V. The electrolysis was carried out at 2000 A, with the voltage decreasing from 12.0 to 8.1. The cathode temperature thermocouple became inoperative during the run, and cathode cooling was poor throughout the run. Electrolysis control temperature was 725°C., and the run was terminated after 5700 ampere hours. A deposit weighing 21 pounds was withdrawn from the cell. The deposit dimensions of 16" length by 6" diameter indicate that the bottom section of the deposit must have dropped into the crucible.

Electrolysis Number III.

Turn-around time between runs No. 2 and No. 3 was one hour and twenty-five minutes. Charge for this run was fifty pounds of Cell Feed 378-1 and six pounds of NaCl. The bath depth was thirty inches. Polarization was at 400 A and 6.2 V for ten minutes, and the electrolysis was carried out at 2000 amps, with the voltage at 14.5 V initially. Cathode cooling was fairly poor throughout the run. The run was terminated at 6200 amp. hours, and

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the deposit resulting from this electrolysis weighed twenty-six pounds. Deposit dimensions were 18" in length by approximately 7" in diameter. It appeared that considerable deposit loss had occurred along the sides of the deposit.

Electrolysis Number IV.

Make-up charge for this run was fifty pounds of Cell Feed 378-1 and six pounds of NaCl. The cathode was preheated to 370°C and polarized at 400 A and 4.7 V. for eighteen minutes until a cathode temperature of 680°C was reached. Electrolysis was carried out at 2000 A. with the voltage decreasing from 11 volts to 7.6 volts. Cathode cooling was insufficient during most of the run. To eliminate chlorine leakage between the stationary and revolving plates of the removal chamber assembly, a check valve in the chlorine outlet line was removed entirely and the sealing liquid was drained from the chlorine outlet. The liquid seal between the stationary and revolving plates was refilled, and no further chlorine leakage between the plates was noted for the remainder of the run. Electrolysis was terminated after 7750 amp. hours. The cathode deposit weighed forty pounds and measured 19" in length by 7-8" in diameter. The outside structure of the deposit was fairly open and some yellowish-white spots were noted on the surface. In general, the deposit was fairly symmetrical, except for some losses along the sides. The bath contained approximately seven per cent Th after this electrolysis.

Electrolysis Number V.

Make-up charge for this run was fifty pounds of Cell Feed (42.9% Th)

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and six pounds of NaCl. Bath depth was 31 inches. Polarization was at 450 A and 4 V for ten minutes. Cathode cooling was very effective during this electrolysis. Electrolysis conditions were 2500 A at 11.0 to 8.4 V. The electrolysis was terminated after 8100 amp. hours. Total deposit weight was 57 pounds. The deposit dimensions were 21 inches in length by 8-1/2" in diameter. There was a slight necking at the top portion of the deposit. The deposit exterior was partially covered with a white material, and the layer of the deposit immediately adjacent to the cathode consisted of solidified salt plus metal for a distance of 1-1/2 inches. The outer inch layer of deposit had a fairly open structure. A sample of bath following electrolysis showed almost no thorium content. The slide valve was not closed after pulling this deposit. Thirty-five minutes after withdrawal of the cathode from the cell, the cathode temperature was 315°C. After one hour of cooling, the temperature dropped to 210°C, and after one hour and thirty-five minutes the cathode temperature reached 80°C. This rate of cooling was fairly representative for all of the runs.

Electrolysis Number VI.

The make-up charge for this run was fifty pounds of cell feed and six pounds of NaCl. Bath depth was thirty-one inches. The cathode was preheated to 300°C and polarized for five minutes at 450A and 4.6 V. Electrolysis was carried out at 2500 A, with the voltage ranging from 12.2 V to 9.2 V. At 6150 amp. hours, the voltage rose from 9.2 to 9.5, and the current dropped to 2400 amps. Electrolysis was terminated at this point.

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Cathode cooling was poor through most of this run. A deposit weighing twenty-six pounds was obtained. It was 14 inches long, and the diameter ranged from nine inches at the top to six and one-half inches at the bottom, indicating a large deposit loss. The deposit surface contained numerous cavities and was covered with yellowish-white salt. When the deposit was raised from the cell, a part of the cathode support clamp broke off. The nickel slide valve was closed while welding repairs were made on the clamp. Hold-up time was forty-five minutes. Thorium concentration of the bath following electrolysis was four per cent.

Electrolysis Number VII.

Make-up charge for this electrolysis consisted of sixty pounds of cell feed and seven pounds of NaCl. The cathode was preheated to 300°C and polarized for ten minutes at 400 A and 5.2 V. The first fifteen minutes of electrolysis were carried out at 1200A. Recurring trouble with the fiberglass-sleeve covered 14 ga. thermocouple wire used for cathode temperature determination necessitated the substitution of 20 ga. thermocouple wire, and no further trouble was encountered in subsequent runs. Electrolysis was continued at 2500 A, with the voltage decreasing from 11.7 V to 9.1 V. At 5800 amp. hours the voltage rose from 9.1 to 9.4, with probable accompanying deposit loss. At 8300 amp. hours the current dropped from 2500 A to 2400 A. Final voltage reading was 9.7 volts. Cathode cooling was poor throughout the run.

Electrolysis was terminated after 8100 amp. hours. The deposit was 16 inches long and tapered from 7-1/2 inches diameter at the top to

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six inches at the bottom. A large portion of the bottom and some of the sides appears to have been dropped.

Electrolysis Number VIII.

Turn-around time between runs VII and VIII was 45 minutes. The make-up charge consisted of sixty pounds of cell feed and twenty pounds of NaCl. The cathode was polarized for ten minutes at 400 A and 5.7 volts. Electrolysis was carried out at 2000 A, with an initial voltage of 9.5 volts. During the run a voltage rise from 7.6 to 7.9 indicated loss of deposit at one point but the run was continued for another 3000 amp. hours to a total of 9850 amp. hours. Cathode cooling was fair throughout the run. Prior to pulling the cathode, argon flow to the removal chamber was increased from 3 CFH to 50 CFH. A deposit weighing 39 pounds and ten ounces was recovered from the electrolysis. It was 18 inches long and seven inches in diameter. Apparently a part of the bottom and sides was lost. The surface of the deposit was contaminated with a very small amount of white and yellowish material.

Electrolysis Number IX.

Make-up charge for this run was fifty pounds of Cell Feed and six pounds of NaCl. Bath depth was 31 inches. Between charging the cell and starting electrolysis, the crucible wall thermocouple used as electrolysis temperature control became inoperative, and the measurement of the crucible wall outside temperature was used as a guide for all subsequent runs. The cathode was polarized for eighteen minutes at 400 A and 5 V until a cathode temperature of 700°C was reached. Electrolysis was started at 2500 A and

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11.5 V. Cooling was very good throughout this run.

At 5300 amp. hours a voltage rise of 0.2 volts was observed, and DC was cut to 2000 amps. at 8.2 volts. At 6300 amp. hours an attempt was made to raise the DC back to 2500, but a small voltage rise was noted immediately, and the run was terminated. For pulling the deposit and subsequent cooling, the argon flow to the removal chamber was increased to 30 CFH. Color of the deposit was black. It weighed forty pounds and was 18 inches long. Diameter of the deposit was seven inches except for a section at the top. The deposit sides appeared to be intact. If any deposit was lost, it appears that it must have dropped from the bottom. The bath sample following electrolysis showed essentially no thorium present.

Electrolysis Number X.

Make-up charge was seventy pounds of Cell Feed. The electrolysis started at 2500 A and 10.8 V, but was changed to 2200 A and then to 2000 A at 9.0 V when analytical results pointed to a low thorium content of the bath at the end of run No. 9. Cathode cooling was well under control throughout the electrolysis. The bath temperature was lowered 10°C during this run because of a slight increase in KCl content of the bath. At 8200 amp. hours the voltage increased from 7.3 to 7.4 volts, and the run was terminated. Argon flow to the removal chamber was 50 CFH when the deposit was pulled. The deposit weight was 56-1/2 pounds, and the dimensions were 23-1/2 inches in length and 7-1/2 inches to 9 inches in diameter, tapering to the bottom.

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Extending below the bottom portion was a three inch long section approximately one and one-half inches in diameter. Apparently there was no deposit loss. There was no white and only a minimum of yellowish surface contamination. Surface structure of the deposit was loose and dendritic at the top, while solid knobs of compact structure were formed on the lower two-thirds of the deposit. The inside structure showed a layer of solid metal plus white salt at an average thickness of one inch next to the cathode. The remainder of the deposit was black in color.

Electrolysis Number XI.

Just prior to adding the make-up charge to the bath, an "O" ring between the stationary and rotating plates of the removal chamber assembly jammed the plates and the electric hoist also jammed. Necessary repairs caused three hours of down-time. The make-up charge for this electrolysis consisted of sixty pounds of cell feed and ten pounds of NaCl. Bath depth was 33 inches. Because of a continuing slight increase in KCl content of the bath, the control temperature was lowered 15°C. Polarization was carried out at 400 A and 5.9 V for 27 minutes while the chlorine scrubber solution was being changed. Cathode temperature at the start of electrolysis was 695°C. Electrolysis current was 2500 A until 5850 amp. hours, when the current was lowered to 2000 amps. because of a voltage rise of 0.2 volts. The electrolysis was terminated at 6500 amp. hours. Cathode cooling was fairly ineffective throughout most of the run. The deposit obtained in this electrolysis was fifteen inches long and very irregular in shape, indicating

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definite deposit loss of both bottom and sides. Color of the deposit was a dark gray, possibly indicative of sodium formation as a result of bath depletion.

Electrolysis Number XII.

Make-up charge for this electrolysis was 103 pounds of Cell Feed and 1-1/2 pounds of NaCl. Bath depth prior to electrolysis was approximately 36 inches. The cathode was polarized for eight minutes at 400 A and 5.7 volts. Later examination of the cathode showed that it was immersed in the bath to a depth of approximately 1-1/2" more than desired. Electrolysis was carried out at 2500 A up to 4200 amp. hours, at which time the DC was cut to 2000 A. A further cut to 1500 A was made after 6800 amp. hours. The run was terminated at 9900 amp. hours. Final DC was 1500 A at 6.4 volts. Cathode cooling was only fair until the DC was dropped to 1500 A. The deposit obtained in this electrolysis weighed 47 pounds. Its diameter was nine to ten inches, and it was approximately 18 inches long, not counting a three inch long by two inch diameter growth at the bottom. In general, the surface was dendritic and covered with a slight amount of yellowish contamination. A portion of the bottom appeared to have been dropped. A sample of the bath taken near the top, showed approximately four per cent of Th, while a sample taken at the bottom showed almost eight per cent Th.

Electrolysis Number XIII.

Make-up charge for this electrolysis was seventy-five pounds of

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Cell Feed and five pounds of NaCl. Bath depth was approximately 35 inches. The cathode was polarized for 26 minutes at 425 A and 5.0 volts until it reached the proper operating temperature. DC current was 2500 A during the first 5200 amp. hours, then cut to 2000 A for the next and final 1000 amp. hours. Cathode cooling was good and easily controlled throughout this run. The electrolysis was terminated when a slight voltage rise was indicated. A sample of the bath taken near the top showed no thorium present. The bath level had dropped to 31 inches after removal of the deposit. The deposit obtained in this run was twenty inches long and approximately 7-1/2 inches in diameter. Its weight was 48-1/2 pounds. It was uniform and symmetrical and was contaminated with only a very small amount of surface oxidation. There was very little dendritic structure evident. A very smooth structure at the bottom was indicative of some possible deposit flow. It appeared that a portion of the bottom may have been dropped.

Electrolysis Number XIV.

Make-up charge for this run was sixty-five pounds of Cell Feed. The cathode was polarized for nineteen minutes at 400 A and 5.1 volts. 635°C was the cathode temperature at the start of electrolysis, and DC was 2000 A throughout the run. Initial electrolysis voltage was 12.2, dropping to 8.5 but rising to 9.0 volts to cause termination of the run at 5300 amp. hours. At the conclusion of electrolysis, the deposit was polarized for

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eight minutes at 450 A and 4 volts, then pulled from the cell. The nickel slide valve was closed and the cell was then shut down. The deposit resulting from this run was dendritic in structure at the top, smooth at the bottom. Its length was only fourteen inches, making it apparent that almost the entire bottom had been dropped. The bottom of the cathode was almost visible. Diameter of the deposit was 7-1/4 inches. There was no solid salt-metal layer next to the cathode, confirming that cooling was inadequate throughout the electrolysis. Weight of the deposit was 23-1/2 pounds.

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MARK VI ELECTROLYTIC CAMPAIGN, MARK VI-87-9

1. Equipment Modifications

Several equipment modifications were made between campaigns to obviate some of the operating difficulties encountered during the June campaign.

The after-cooler for the compressor which supplied cooling air for the cathodes was completely overhauled. It was found that a considerable portion of the water cooling tubes had become fouled, explaining in part the erratic performance of the cathode air cooling system during the June campaign. To prevent oil from entering the cooling air flow meter and giving rise to false readings, an oil trap was placed in the line just ahead of the flow meter. Provision was made for additional cooling of the air should this prove necessary. During the Mark VI-87-8 campaign, the cathode cooling air was allowed to escape from the top of the cathode directly into the operating area. For the December campaign the cooling system was revised to pipe the exit cooling air to an outside vent.

The stationary and rotating plates of the removal chamber system were modified, straightened, and remachined. The stationary plate had warped during the June campaign; this warpage permitted chlorine to escape between the stationary and rotating plates and made the liquid seal on the chlorine take-off system inoperative. To overcome the warpage, the plate was first straightened in a press and then remachined. The bottom surface of the rotating plate was re-clad with a nickel sheet, and the plate

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itself was strengthened by adding a bridge-type angle iron brace on top to prevent future warpage. The neoprene "O" rings between the plates were replaced by slightly larger diameter stock.

The bottom of the Graphitite crucible was lined with one inch alundum slabs to reduce carbiding of any thorium metal deposits dropped during the course of electrolysis and, if possible, to modify the DC current path so as to grow shorter deposits.

To prevent splashing into the heating element zone during the charging operation, two semi-circular graphite segments were placed on top of the crucible, reaching almost to the neck section leading to the removal chamber assembly. Because of operating difficulties described below these splash shields had to be removed from the cell before the next campaign got under way, however.

A thermocouple well was drilled through the crucible wall so that the bath temperature could be measured directly, rather than using the crucible wall temperature as control temperature, as was done in the previous campaign.

The liquid seal between the stationary and rotating plates of the removal chamber assembly consisted of a high viscosity gear oil, and the liquid seal in the chlorine take-off system consisted of a low viscosity oil maintained at the proper depth to hold the entire system at a positive pressure of about two inches of water.

A recording voltmeter was installed. Several minor re-piping jobs and similar items completed the system modifications for the ensuing campaign Number Mark VI-87-9. The Mark VI electrolytic cell was

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evacuated at both low and high temperatures and was ready for operation by November 29, 1955. The cell itself was evacuated to 175 microns, and the removal chamber system to 28.5 inches Hg.

2. Standard Operating Procedure for Mark VI Electrolytic Cell

As far as possible, a standard operating procedure was adhered to during the ensuing campaign. Rather than describe each individual electrolytic run of the campaign in detail, the standard operating procedure followed during these runs is given below:

As a starting point it is assumed that the Mark VI assembly will have been completed, one cathode removal chamber and its accompanying cathode being in position over the cell ready to be inserted, with the other cathode plus removal chamber in the cooling position.

1. Make water cooling and air connections at the electrolyzing cathode top.
2. Attach DC power clamp and polarizing cable to cathode.
3. Turn DC power on polarizing (300 amperes at whatever voltage is necessary, but ascertaining that the polarizing voltage is at least 3.5 volts) and increase argon flow to removal chamber to approximately 2.5 liters per minute.
4. Open the nickel slide valve and lower the argon-actuated cylinder pistons.
5. Lower the cathode into the cell, to a level somewhat above the bath (see measurement card at operator station), and pre-heat to approximately 300°C. The bath temperature should be in the range of 735-755°C.
6. Lower the cathode into the bath, to a position where the tip plus 2-1/2" of shaft length are immersed in the bath. Attach the three large DC power cables. Note the bath depth when lowering the cathode, this being a current surge in the DC circuit. Leave the DC power

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at polarizing level until the cathode reaches the temperature between 675-700° C. Maintain a small flow of cooling water during this entire cyclic operation in the cathode water jacket. Check for steam at the drain manifold.

7. Start cooling air to cathode. Increase DC current to 2,000 amperes (or other specified amperage) when the cathode operating temperature has been reached.
8. Cooling air should be adjusted during run to obtain cathode temperatures as follows: At the start, 675-700°C. By 2,000 ampere hours, a level of 625°C. Following this, the cathode temperature should drop steadily at a rate of approximately 10°C per 500 ampere hours.
9. Terminate the electrolysis after 7,500 ampere hours (or other specified limit) by decreasing the DC current to a level of 300-400 amperes.
10. Maintain the deposit under polarizing conditions in the bath for at least ten minutes but no more than fifteen minutes in order to establish thermal equilibrium in the deposit and give it greater strength prior to raising.
11. During the course of electrolysis it is assumed that the other cathode will have been removed from the cooling chamber after having been cooled to less than 100°C, chipped, replaced in the removal chamber, the assemblage set in place, the chamber evacuated and flushed with argon. Neither cooling air, water or power leads will have been attached to this assemblage at this point, however. The inside of the removal chamber should be washed down with acetone prior to the evacuation and flushing operation.
12. Increase the flow of argon to the removal chamber over the cell to a level of 30 cu. ft./hr. approximately five minutes before the cathode is to be withdrawn. Initiate cooling water to the removal chamber jacket, remove the three large DC cables from the clamp, and slowly raise the cathode out of the bath in a uniform manner until it is resting inside the removal chamber at the proper level. Cut all DC power to the cathode and remove the polarizing cable and DC clamp. Increase argon flow to cell while pulling deposit, to maintain positive cell pressure.
13. Raise the argon-actuated cylinder pistons and close the slide valve.

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DISCUSSION OF ELECTROLYTIC OPERATIONS, MARK VI-87-9 CAMPAIGN

The prime purpose of this campaign was to serve as a final shakedown run for several equipment modifications and operational changes intended for use on a subsequent commercial prototype electrolytic cell (Mark XXVI).

1. Campaign Summary

The results obtained in this campaign showed the effectiveness of equipment modifications made prior to the campaign. For example, the average cathode deposit weight increased from 38.1 pounds in the first campaign to 51 pounds in the second campaign. The average amount of thorium metal (not including fines) increased from 15.6 pounds to 20.7 pounds, and average current efficiency (not including fines) increased from 44.5 per cent to 59.5 per cent. Striking improvement was also made in the quality of metal produced. This is discussed in greater detail below.

The campaign proved the feasibility of the removal chamber system both from the viewpoint of the semi-continuous operation concept as well as a means of maintaining an inert electrolytic cell atmosphere. Cathode cooling was shown to be an effective means of preventing cathode deposit loss. These and other modifications are discussed below.

A campaign summary is presented in Table V, and an analysis of individual electrolyses is given in Table VI.

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Summary of Results, Mark VI-87-9 Campaign

Total cathode deposit weight	660-3/4 pounds
Total thorium metal recovered from deposits	328-1/2 pounds
Average per cent metal in deposits, including pro-ration of fines	49.7%
Average per cent metal in deposits, not including fines	40.5%
Total thorium recovered as metal, including 668 g. of metal recovered from crucible	330.0 pounds
Total ampere hours for campaign	95,150 amp.hours
Campaign current efficiency	72.8%
Individual run average efficiency	* 59.5%
Process yield, including fines	86%
Process yield, not including fines	71%
Total number of cathode deposits produced	13
Average approximate electrolytic cycle time	7 hours
Average electrolysis time per cycle	3.8 hours
Thorium metal production rate per hr. of electrolysis	6.75 lbs./hr.
Approximate initial cathode current density at 2000 amp. operating level	235 A/dm ²

The campaign current efficiency of 72.8 per cent compares favorably with results of smaller scale electrolytic runs previously reported by Horizons Incorporated. Overflow fines from the metal washing

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equipment were collected in toto, i.e., no attempt was made to separate and weigh the fines from the various electrolytic runs. Therefore, the current efficiency figures available for individual runs are based on metal recovery from the deposit exclusive of fines.

Table VI

Analysis of Individual Electrolyses in Mark VI-87-9 Campaign

Electrolysis Number	Th charged Prior to Run lbs.	Total Amp Hrs.	Approx. Duration Hrs.	Crushed Deposit Wt. -lbs.	*Washed Metal Wt. -lbs.	*Metal in Dep. %	*Current Efficiency %
1	56-1/4	7500	3-3/4	60-1/4	22.6	37.5	63
2	30	6500	3-1/4	51	17.6	34.5	57
3	30	7500	3-3/4	48	22.5	46.8	63
4	30	7050	4-1/2	40-1/2	19.8	48.9	58
5	30	10,000	5	63	27.6	43.8	58
6	40	8000	4	55-1/2	27.7	49.9	73
7	None	9050	4-1/2	31-1/2	12.4	39.4	28
8	30	7000	3-1/2	48	17.9	37.3	54
9	40	8000	4	60	27.0	45.0	71
10	20	6050	3	49-1/2	17.0	34.4	59
11	30	6000	3	57	21.4	37.6	75
12	32	7500	3-3/4	53-1/2	24.6	46.0	69
13	14-1/2	5000	3	43	10.9	25.4	46

* This does not include the fines which were recovered for the campaign as a whole.

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The two runs with the lowest individual efficiencies were run under adverse conditions which should not be encountered under actual plant operating conditions. For Run No. 7 no thorium make-up was added, and Run No. 13, the final run of the campaign, was essentially run to the thorium depletion point. Conditions in neither run were conducive to high current efficiencies. If both of these runs are discounted, the individual run average efficiency becomes 63.6 per cent.

The individual run average efficiency may actually be a more reliable indication of process efficiency than the overall current efficiency figure, since fines in general represent metal of lower quality and may possibly have to be recycled.

The process yield for this campaign was 86 per cent, i.e., 86 per cent of the thorium values charged to the electrolytic cell were recovered as thorium metal.

Evaluation data of thorium metal produced in this campaign are presented in Tables VII and VIII, and are discussed in another section of this report. "HCl-insolubles" in the metal powder averaged 0.28 per cent, but increased to an average value of 1.20 per cent in melted buttons. Average Rockwell-E Hardness was 68.5, which corresponds to 60.5 Brinell.

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Table VII

Evaluation of Thorium Metal Produced in Mark VI-87-9 Campaign

Electrolysis Number	Time min.	Acid Treatment		HCl-Insolubles		Hardness	
		Acid	Powder %	Button %	Rockwell-E	Brinell	
1	5	1% H ₂ SO ₄	0.38	2.38	97	94.5	
2	15	3% H ₂ SO ₄	0.04	1.80	79	58.6	
3	15	3% H ₂ SO ₄	0.14	1.01	69	51.8	
4	15	3% H ₂ SO ₄	0.11	1.90	76	69.1	
5	15	3% H ₂ SO ₄	0.28	2.00	71.5	64.6	
6	15	5% H ₂ SO ₄	0.04	0.68	60.5	56.8	
7	15	5% H ₂ SO ₄	0.10	*	----	----	
8	30	5% H ₂ SO ₄	0.56	0.85	55	50.3	
9	30	5% H ₂ SO ₄	0.73	0.79	73.5	64.6	
10	30	5% H ₂ SO ₄	0.42	0.97	53	48.9	
11	30	5% H ₂ SO ₄	0.19	0.57	52	47.5	
12	30	5% H ₂ SO ₄	0.32	1.44	78.5	69.1	
13	30	5% H ₂ SO ₄	0.30	1.19	59	50.3	

* Powder contaminated with sodium; would not melt.

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Table VIII

Typical Screen Analysis of Thorium Metal

(Ref. Mark VI-87-9) (Run 9)

<u>On Tyler Screen No.</u>	<u>Cumulative Per cent</u>	<u>Individual Per cent</u>
20	9.2	9.2
70	63.5	54.3
100	79.1	15.6
140	89.0	9.9
170	89.6	0.6
200	94.0	4.4
-200	100.0	6.0

Table IX

Spectrographic Analysis of Typical Electrolytic Thorium Powder

Produced in Mark VI Cell

Th	Major
B	< 0.4 ppm
Si	20
Fe	20
Mg	< 10
Al	11
Ni	25
Cd	< 0.5
Zn	< 10
Mn	< 10
Pb	< 10
Sn	< 10
Cu	0.5
Co	< 5

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Table IX (continued)

Cr	15
Zr	< 10
Ti	10
Ca	20
Mo	< 10
W	< 10
V	< 10

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A thorium values material balance is presented in Table X. The thorium metal produced during this campaign accounts for 86.2 per cent of the thorium values charged to the electrolytic cell. Thorium values recovered from the cathode deposit salt matrix, from the spent electrolyte remaining in the crucible at the end of the campaign, and from a dust trap in the chlorine take-off line, account for 5.3 per cent of the initially charged thorium values. The remainder, or 8.5 per cent of the thorium values, was a process loss attributable to thorium tetrachloride volatilization and mechanical carry-over by entrainment in the effluent chlorine gas stream, with subsequent deposition on cell and auxiliary components, absorption of salts into the graphite crucible walls, and absorption of volatilized thorium tetrachloride in the firebrick insulation surrounding the crucible. A portion of the process loss also is attributable to splashing of the electrolyte during the charging operation. Volatilization losses are estimated to be less than three per cent of this total.

The process loss of thorium values is a problem of major importance and calls for more effective means of recovery than have been employed

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heretofore. Thorium salts which have been absorbed in cell components such as crucibles and firebrick are, of course, recoverable when the equipment is dismantled during routine preventive maintenance shutdowns common to production plants. The problem of electrolyte splashing can be minimized by a relocation of the feed make-up port and by continuous feeding instead of batch-wise charging. Some thorium values were recovered during the campaign by the use of a dust trap in the chlorine take-off line. Major emphasis must therefore be placed on efficient recovery of thorium values from dust and volatilized thorium chloride condensate deposition on the upper structure of the cell and auxiliary components.

Table X
Thorium Values Material Balance, Mark VI-87-9 Campaign

Total weight of thorium charged to cell	382.7 pounds
Thorium recovered as metal in individual runs	269.0 pounds
Thorium recovered as metal fines, campaign total	59.5 pounds
Thorium recovered as metal in the crucible bottom	1.5 pounds
Thorium recovered from the deposit salt matrix	16.4 pounds
Thorium recovered from spent electrolyte chipped from the crucible	3.2 pounds
Thorium recovered from chlorine line dust trap	0.5 pounds
Total thorium recovered	350.1 pounds
Thorium losses *	32.6 pounds
Process loss - per cent thorium	8.50 per cent

* Losses by ThCl_4 volatilization, entrainment in Cl_2 gas stream, splashing during the charging operation and absorption by cell components.

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2. Removal Chamber and Charging System

The modifications and repairs made on the removal chamber supporting plates prior to this campaign overcame the operating difficulties encountered in the removal chamber system during the first campaign.

In general, the removal chamber system appeared to give satisfactory protection to the cell atmosphere. The majority of the cathode deposits produced in this campaign were black in color, which is indicative of a good (i.e., inert) cell atmosphere. No yellowish or whitish surface contamination, such as was common during the early runs of the first series, was found on any deposits produced in this series.

A good seal was obtained around each removal chamber between the plates, shown by the fact that a sight glass in the top plate remained clear throughout the campaign. A poor seal would have permitted diffusion of chlorine and dust between the plates and would have made observation through the sight glass impossible after the first run. It was possible to evacuate the chambers to 27 to 28 inches of vacuum between runs so they could be argon-flushed prior to re-use.

The beneficial effect of the improved cell atmosphere is dramatically illustrated by a comparison of "HCl insolubles" data of the first and second Mark VI campaigns. "HCl insolubles" is for the most part constituted of high-temperature thorium oxide, which forms a refractory, very stable thorium oxide upon irradiation of the material. The data presented in Table XI show that thorium powder produced in the first campaign had an average "HCl insolubles" content of 1.20 per cent in the powder, compared

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to an average value of 0.28 per cent for the second campaign.

Table XI

Comparison of Thorium Metal Produced in Mark VI Campaigns

Electrolysis Number	HCl Insolubles in Th Powder - per cent		Hardness Rockwell - E	
	1st Campaign	2d Campaign	1st Campaign	2d Campaign
1	2.12	0.38	----	97
2	0.62	0.04	----	79
3	1.27	0.14	60	69
4	0.79	0.11	52*	76
5	0.64	0.28	74	71.5
6	0.84	0.04	----	60.5
7	1.17	0.10	64*	----
8	0.99	0.56	----	55
9	1.36	0.73	68	73.5
10	1.27	0.42	74	53
11	1.35	0.19	63	52
12	1.25	0.32	76	78.5
13	1.75	0.30	85	59
14	1.33	----	68	----
Avg.	1.20	0.28	----	----

* Rockwell-B Scale

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It is interesting to note that hardness tests are not indicative of "HCl insolubles" content of thorium metal. For example, metal produced in the third run of the Mark VI-87-8 campaign had a hardness of R_E-60 and an "HCl insolubles" content (in metal powder) of 1.27 per cent, while metal from the fifth run had a hardness of R_E-74 , but contained only 0.64 per cent "HCl insolubles."

The improved seal between the stationary and rotating plates of the removal chamber system also enabled the liquid seal in the chlorine take-off line to perform properly in this campaign. It was possible to maintain the liquid seal throughout the campaign and so to maintain the cell atmosphere at a positive pressure of approximately two inches water gauge. The liquid seal prevented back-diffusion of air into the cell via the chlorine take-off line.

The substitution of a high-viscosity gear oil for the low-viscosity oil formerly used in the rotating plate periphery liquid seal improved the operability of that seal by reducing the tendency to splash oil out of the seal when lowering the rotating plate to its "down" position.

The charging system operation still left something to be desired. Splash shields atop the crucible had to be removed even before the campaign got under way, since they interfered with lowering of the cathode into the bath. A possible reason for the interference may be a slight pendulum effect which occurs as the cathode is being lowered. The pendulum effect causes heat shields which are attached to the cathode to strike the splash shields in the crucible.

It was observed that the cell pressure tended to become negative during

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batch charging of cell feed. To prevent contamination of the cell atmosphere it is desirable, of course, to maintain a slight positive cell pressure at all times. Temporary expedients for overcoming this difficulty during the campaign were slow, step-wise if necessary, charging of the feed and increased argon flow to the cell. By operating in this manner it was possible to maintain a positive cell pressure during the charging operation.

Both of the charging difficulties described above are being remedied by appropriate design changes on a commercial prototype cell presently under construction.

3. Cathode Cooling System

The Mark VI-87-9 campaign again demonstrated cathode cooling to be a major factor in the success or failure of thorium electrolysis. As pointed out before, effective cathode cooling tends to prevent loss of metal deposit during electrolysis. For the most part, the cooling system operated effectively during this campaign, and deposit loss was held to a minimum. The amount of thorium metal recovered from the crucible at the end of this campaign was only 668 grams, compared to 42.5 pounds recovered upon termination of the previous campaign. It is recognized that neither of these quantities necessarily represents the full amount of thorium dropped from cathode deposits, since part of the dropped metal deposit may either have been re-chlorinated or carbided by contact with the graphite crucible. Nevertheless, the comparison of relative amounts

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of metal recovered from the crucible, in conjunction with cathode temperature observations made during the campaign, bears out the contention that the cathode cooling system operated effectively during the Mark VI-87-9 campaign. Over-hauling the air supply after-cooler prior to the campaign resulted in preventing the air flow meter from becoming partially filled with condensed moisture which occasionally would have made it impossible to obtain adequate cooling air flow.

4. Other Modifications

It was alluded to above that carbiding of dropped metal deposits may take place by contact of the metal with the graphite crucible. To a large extent this was prevented during the last Mark VI campaign by an alundum slab lining on the bottom of the crucible. It was hoped, prior to the campaign, that the alundum slab lining would also have an effect on the DC current path in the Mark VI cell and that it would modify the DC path so that shorter metal deposit growth would result.

It had previously been shown that cathode deposits tended to grow to a length approximately 150 per cent that of the cathode-tip length. This characteristic growth may be attributed in part to the DC current path, since the anode connection in the Mark VI cell is made at the crucible bottom. Cathode deposit growth to a considerable distance below the cathode-tip extremity leads to poor cooling of that part of the deposit and may result in deposit deformation, flow, or loss, since cooling of the cathode deposit becomes ineffective beyond a distance of approximately

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2-1/2 inches from the cathode surface. Placing the alundum slab lining on the bottom of the crucible was an attempt at forcing a larger portion of the DC current to travel along the side walls of the crucible and so to alleviate the undesirable cathode deposit shape.

To determine the effectiveness of the alundum lining, several of the first campaign deposits which were cooled effectively and presumably showed no deposit loss were compared to deposits from the second campaign, comparison being made between runs of approximately equal duration ($\pm$ 500 amp. hours). For the runs of approximately 6000 amp. hours duration, deposits in an unlined crucible grew to an average of 18 inches in length, while deposits in the alundum-lined crucible averaged 16-1/2 inches in length. For runs of approximately 7500 amp. hours duration, deposit length in the unlined crucible averaged 22 inches, while deposits in the lined crucible averaged only 18 inches in length. It may then be tentatively concluded that the alundum lining proved effective in reducing overall cathode deposit length.

A recording voltmeter was utilized for the first time during the Mark VI-87-9 campaign to provide a written record of DC voltage during electrolysis. It proved to be a valuable control instrument since it visually portrays by a voltage rise when an end point has been reached and therefore signals when an electrolysis should be terminated. During the campaign the signal was not necessarily obeyed, i.e., several runs were continued at lower DC current levels until another end point signal was obtained. Subsequent results, however, showed that the runs should

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have been terminated at the first end point indication, with resulting higher current efficiencies.

The recording voltmeter also gives a second type of signal to call for termination of electrolysis. In general, DC voltage drops at a steady rate throughout the electrolysis. When the voltage remains at a constant level instead of dropping, it may indicate that bath concentration is too low for efficient electrolysis. For example, in Run No. 7 of this campaign, the voltage remained constant for the last 6000 amp. hours of a 9000 amp. hour total run. Current efficiency for this run was by far the lowest of the campaign, only 28 per cent.

Prior to the campaign a thermocouple well was positioned directly in the bath to provide closer process control of bath temperature. Unfortunately the thermocouple burned out during the second electrolysis of the series and could not be replaced. As pointed out before, the construction of the Mark VI cell and its adaptation to a removal chamber system made it impossible to replace thermocouples once a campaign got under way. Temperature control of the operation was subsequently based on a temperature reading of the outside crucible wall temperature and occasional bath temperature spot checks made by immersing the bare cathode in the bath, allowing it to reach thermal equilibrium with the bath, and reading the resulting cathode temperature.

No particular effort was made during this campaign to maintain the NaCl-KCl ratio constant throughout the run. The cell feed available for make-up charges analyzed only 40 per cent thorium content. As pointed out above, a cell feed of at least 45 per cent thorium content is necessary if

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it is desired to maintain the NaCl-KCl weight ratio in the electrolyte at 2:1 and if no increase in bath depth is to occur during a continuous electrolytic campaign. For the most part, the make-up charges during this campaign were intended to replace thorium values removed from the electrolyte during the previous electrolytic cycle, without unduly raising the level of electrolyte in the crucible.

5. Manpower and Time Requirements

During the Mark VI-87-9 campaign a three-man crew was used for cell operation, and for one 8-hour period only a two-man crew was available. The two-man reduction in crew personnel brought about an increase in turn-around time between electrolyses to approximately a three-hour average, compared to approximately a two-hour average with a five-man crew during the previous campaign. Due to mechanical difficulties a six hour shut-down was necessary and this time was omitted in figuring average turn-around time.

The average turn-around time is not necessarily indicative of actual time requirements between electrolyses. For example, turn-around times of as little as 45 minutes were experienced during the Mark VI-87-8 campaign. In general, the major time requirement between electrolyses was the time spent in sampling the bath, adding the make-up charge, and waiting for the make-up to melt down prior to proceeding with the next electrolysis.

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INDIVIDUAL ELECTROLYTIC RUNS, MARK VI-87-9 CAMPAIGN

Cell heat-up started at 0815 hours on November 29, 1955. A final check-out lowering of the cathode into the cell disclosed that the splash shields on the crucible interfered with cathode movement, possibly due to a slight pendulum effect during cathode lowering. The heat-up was therefore terminated after three hours and the cell allowed to cool down to permit removal of the splash shields.

On December 1, 1955, the cell was re-evacuated, flushed with argon, and heat-up started at 1530 hours. The cell reached operating temperature after 12-1/2 hours and the first portion of the initial charge was dropped to the cell approximately one-half hour later. Over a period of eleven hours the entire charge of 375 pounds was charged and melted.

The initial charge constituted a bath of 29.5 inches depth, with a 15 per cent thorium concentration. The thorium value was supplied as cell feed of 26.3 per cent thorium content, the thorium being in the form of thorium chloride. The remainder of this cell feed was composed of an eutectic mixture of sodium and potassium chlorides. The total initial charge of 375 pounds was composed of 214 pounds of this cell feed and 161 pounds of sodium chloride. Density of the molten charge was approximately 0.065 lb./cu.in.

Electrolysis Number I

The cathode was preheated and polarized at 300 amps and 3.5 volts. DC current during electrolysis was 2000 amps, with the voltage dropping

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from an initial value of 9.6 volts to a final value of 6.8 volts. Cell pressure throughout the run was maintained at approximately 1.5 inches of water. Cathode cooling appeared to be effective throughout the run; at the termination of electrolysis the cathode temperature was 535°C. Cooling air flow averaged about 1300 CFH. The electrolysis was terminated at 7500 ampere hours, and the cathode was polarized for fifteen minutes at 350 amps and 3.5 volts with continued air cooling. The cathode tip temperature was 500°C when the cathode was pulled out of the bath. The first cathode deposit weighed 60-1/2 pounds. It was twenty inches long and approximately ten inches in diameter. It was symmetrical and uniform in appearance, black in color, and had a rather porous-structured shaggy outer surface. Thorium content of the bath following electrolysis was eleven per cent.

Electrolysis Number II

Make-up charge for this run was 75 pounds of sodium chloride-potassium chloride eutectic cell feed containing forty per cent of thorium as thorium chloride. Bath depth after the make-up addition was 29.5 inches. The electrolysis was carried out at a DC level of 2000 amps, with the voltage dropping from 9.6 to 7.3 volts. Cell pressure averaged approximately 1.8 inches. For reasons unknown, the DC current rose to 3000 amps at one point of the run. The electrolysis was terminated at 6500 amp hours, and the cathode was

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polarized as before. Cathode tip temperature was 590°C when the cathode was pulled. A partial vacuum was pulled on the cell as the deposit was being raised. This occurrence was overcome in later runs by increasing argon flow to the cell while the deposit was being raised into the removal chamber. Shortly after termination of this run, the bath thermocouple became inoperative, and the crucible temperature was used as control temperature for the remainder of the campaign. Bath temperature was checked occasionally by allowing a bare cathode to come to thermal equilibrium with the bath and measuring the cathode temperature. Deposit No. 2 weighed 51 pounds. Its approximate diameter was ten inches, its length was 18 inches. Color of the deposit was black, and its surface was dendritic in structure. One side of the deposit appeared flattened. Thorium content of the bath after electrolysis was eleven per cent.

Electrolysis Number III

Make-up charge for this run was 75 pounds of 40 per cent Th cell feed. Initial bath depth was 32 inches. The electrolysis was again carried out at 2000 amperes, with the voltages dropping from 11.5 to 7.4 volts. Cell pressure averaged two inches. Cathode cooling was satisfactory throughout the run. Average cooling air flow was 1400 CFH. The electrolysis was terminated at 7500 amp hours. The deposit was approximately ten inches in diameter and 14 inches long, with a three inch wide by four inch long appendage at the bottom. The top of the

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cathode appeared not to have been immersed in the bath. Deposit weight was 49 pounds.

Electrolysis Number IV

Make-up charge for this run was 75 pounds of 40 per cent Th cell feed. Initial electrolyzing current was 2000 amps, which was reduced to 1000 amps after 3300 amp hours to bring cathode temperature under control. After another 850 amp hours, the current was increased to 1500 amps and remained at that level hereafter. The cathode shorted out on several occasions during the run. Cathode cooling was generally unsatisfactory. The compressed air after-cooler was running warm, and at one point water began to accumulate in the air flow meter. The electrolysis was terminated at 7,050 amp hours, and a deposit weighing 42 pounds was obtained. Approximate deposit dimensions were nine inch diameter by 14 inches long. The surface was dendritic in structure, and it appeared that a small portion of deposit might have been dropped. The thorium content of the bath following electrolysis was approximately six per cent.

Electrolysis Number V

Make-up charge for this run was again 75 pounds of 40% Th cell feed. The initial bath depth was thirty inches. At 2000 amps the voltage dropped from 9.2 volts to 7.5 volts over an electrolysis of 10,000 amp hours duration. Cathode cooling was satisfactory, and average cooling air flow was 1700 CFH. The cathode was cooled to 370°C prior to being

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raised out of the bath. Deposit weight was 64-1/2 pounds, and the deposit appeared to contain more salt than usual. It appeared that a portion of the deposit might have been dropped. Color of the deposit was black. It was shaggy in appearance, twenty inches long by ten inches in diameter.

Electrolysis Number VI

The make-up charge for this run was 100 pounds of 40 per cent Th cell feed. The electrolysis current was 2000 amps, at an initial voltage of 9.8 volts and final reading of 7.5 volts. Cathode cooling was satisfactory, with a final cathode temperature of 545°C. However, an air flow of approximately 3100 CFH was required. Cell pressure during the run averaged 2.1 inches. The thorium content of the bath following electrolysis was 12.2 per cent.* The cathode deposit obtained in this run weighed 56 pounds and was eighteen inches long by 9-1/2 inch diameter. Several tentacle-like pieces extended about three inches from the bottom. Duration of the run was 8000 amp hours.

Electrolysis Number VII

The make-up charge for this run consisted of thirty pounds of sodium chloride only. The bath depth was thirty inches. DC current was 2000 amps at 9.2 to 8.1 volts over a run of 9,050 amp hours duration. During the last 6,000 amp hours of the run the voltage remained constant. Cathode cooling was satisfactory and average cooling air flow was 2100 CFH. Average cell pressure was 1.5 inches. The final thorium content

* Due to stratification and sampling difficulties these percentages are only approximate.

of the bath was 7.5 per cent.* Dimensions of the cathode deposit were sixteen inches length by 7-1/2 inches in diameter. There was no evidence of deposit loss, and the deposit was uniform in shape. Weight of the deposit was 33-1/2 pounds.

Electrolysis Number VIII

A make-up charge of 75 pounds of 40 per cent Th cell feed was added prior to the run. The major electrolysis current was 2000 amps, at 9.0 to 7.1 volts. After 7,000 amp hours the voltage rose from 7.1 to 7.6 volts, and the run was terminated. Cell pressure averaged 2.1 inches. Cathode cooling was only fair at a cooling air level of as high as 3000 CFH. Final thorium content of the bath was 4.2 per cent.* The cathode deposit was polarized for twenty-five minutes at 300 amps and 3.5 volts and cooled to 525°C before being raised to the removal chamber. It appeared to be coated with more salt than usual and showed no apparent loss of deposit. Deposit weight was 48-1/2 pounds and deposit dimensions were nineteen inches in length and nine inches in diameter.

Electrolysis Number IX

The make-up charge for this run consisted of one hundred pounds of 40 per cent Th cell feed to bring the bath level to 31 inches. The electrolysis was carried out at a level of 2000 amps. Initial voltage was 9.0 volts, and the final voltage reading was 7.0 volts. Run duration was 8000 amp

* Due to stratification and sampling difficulties these percentages are only approximate.

hours. The AC (heating) power settings for this run were 8 and 25 kw, respectively, as low and high settings of the temperature controller. Average cell pressure was 2.1 inches of water. Cathode cooling was very satisfactory at a cooling air flow of 1200 CFH. Cathode temperature at the end of electrolysis was 505°C. The polarizing period was 29 minutes at 450 amps and 3.7 volts. Thorium content of the bath was 6.2 per cent following electrolysis Number IX. A small amount of free carbon was found in the bath sample. The cathode deposit obtained from this run weighed sixty pounds. It was twenty inches long by nine inches in diameter. Its color was a grayish black, and it was very symmetrical in appearance. The deposit surface was dendritic in structure. It appeared that a slight amount of flaking off the surface had occurred.

Electrolysis Number X

A make-up charge of fifty pounds of 40 per cent Th cell feed was added prior to electrolysis to bring the bath level to 30-1/2 inches. Electrolysis current was 2000 amps. The voltage dropped from an initial value of 9.7 volts to 7.6 volts at approximately 5,800 amp hours, then rose to 8 volts at 6,050 amp hours, and the run was terminated at this point. Cathode cooling was satisfactory at a cooling air flow of 2,300 CFH. Average cell pressure was 2.1 inches. The cathode deposit weighed fifty pounds. It was irregular in shape, with the diameter varying from ten inches to 7-1/2 inches and an overall length of fifteen inches. It appeared that most of the deposit below the cathode tip might have fallen off or did not adhere to begin with, due to sodium formation

on this cathode in Run No. 8. There was physical evidence of sodium formation on cathode deposit No. 10. The deposit surface was dense and covered with small, knobby structures.

Electrolysis Number XI

Seventy-five pounds of forty per cent Th cell feed was charged as make-up. The initial bath depth for this run was 31 inches. Electrolysis current was 2000 amps, with the voltage dropping from an initial 8.6 volts to 7.5 volts after 6,000 amp hours of operation. Cathode cooling was satisfactory, with the average air flow being 2000 CFH. Average cell pressure was 2.3 inches. The deposit was polarized for thirty minutes at 320 amps and 3.5 volts. The deposit weighed 57-1/2 pounds. It was seventeen inches long by nine inches in diameter, uniformly shaped, dark in color and dendritic in surface structure. There was no apparent loss of deposit. Final thorium content of the bath was 9.6 per cent.*

Electrolysis Number XII

The make-up charge for this run consisted of eighty pounds of forty per cent Th cell feed to bring the bath depth to 30-1/2 inches. The cathode tip was cleaned with dilute HCl prior to electrolysis to remove any traces of sodium which might interfere with deposit adherence. Attempts to lower the cathode into the bath were unsuccessful, but there was no evidence of skull formation on the bath. The cathode was withdrawn for inspection and a second cathode was lowered into the cell. After a further

* Due to stratification and sampling difficulties these percentages are only approximate.

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minor difficulty electrolysis was initiated at 3000 amps, but the current was cut back to 2500 amps after four minutes because of fluctuations and further reduced to 2000 amps after another three minutes because of voltage rise. The fluctuations may have been due to the cathode shorting out, which was noticed at this point. However, the electrolysis was continued at a 2000 amp level at an initial voltage of 9.8, dropping to a final value of 7.7 volts. At 7500 amp hours the electrolysis was terminated when the voltage rose by 0.3 volts, indicating an end point. Immediately thereafter, the voltage dropped by 0.5 volts. DC was then cut back to polarizing at 4.3 volts and 580 amps. The polarizing period was fifteen minutes. Average cell pressure during the run was 2.2 inches. Cathode cooling was satisfactory with an average cooling air flow of 2000 CFH. The cathode deposit weighed 53 pounds. It appeared somewhat rectangular in cross section. Deposit dimensions were eighteen inches in length by eight to ten inches in diameter. The deposit shape was irregular and indicated some deposit loss. The surface structure was coarser and more dense than in most of the earlier runs. Color of the deposit was a grayish black.

Electrolysis Number XIII

Only 36 pounds of forty per cent Th Cell feed, representing the remainder of the available cell feed, was charged as make-up. Bath depth initially was 33 inches. Electrolysis was initiated at a level of 2000 amps. After 3800 amp hours, a voltage rise of 0.2 volts was

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noted, and the DC was cut back to 1500 amps. Another voltage rise of 0.2 volts occurred 400 amp hours later, and the current was again reduced, this time to 1000 amps at 5.7 volts. Eight hundred amp hours later, when a total of 5000 amp hours had been reached, the run was terminated. Slight voltage fluctuations were observed throughout the latter portion of the run. Aside from these fluctuations the voltage remained constant, i.e., at a value of 5.7 volts. The polarization period was fifteen minutes at 250 amps and 3.8 volts. Average cell pressure during the run was 2.3 inches. Cathode cooling was satisfactory, but an air flow of approximately 2600 CFH was required. The cathode deposit was sixteen inches long. Its diameter at the upper 2-1/2 inch portion was ten inches, but only eight inches below that point. The surface of the top portion was knobby and of grayish-black color. The lower portion had a glazed surface indicative of sodium formation. Small grayish granular particles indicative of sodium formation were also noted. Directly above the thermocouple well the deposit grew out one inch from the remainder of the deposit in a semi-circular shape. Total deposit weight was 43 pounds.

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APPENDIX

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Procedure:

- 1) Dissolve 20 g sample in water at room temperature.
- 2) Make solution up to 100 ml in volumetric flask.
- 3) Obtain hydrometer reading of resulting solution

Fig. 1

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Fig. 2

Cathode Temperature Vs Ampere Hours
Mark VI Electrolytic Campaigns

- June 1955 Campaign, Electrolysis No. 7
- △— June 1955 Campaign, Electrolysis No. 10
- December 1955 Campaign, Electrolysis No. 9

Fig. 3

DC Voltage Change During Electrolysis
at Constant Current Level of 2000 Amps

Fig. 5

Partial View of Mark VI Electrolytic Cell
Showing Slide Valve and Removal Chamber
System in Place

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Fig. 6

Rotating Support Plate and Removal
Chambers Prior to Assembly

Fig. 7

Rotating Support Plate, Removal Chambers,
and Charge Hopper Prior to Assembly

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Fig. 8

Top View of Removal Chamber System, With a Cathode Positioned in One Chamber. The Charge Hopper is not Shown in This View.

Fig. 9

Partial View of Control Panel, Mark VI Electrolytic Cell

Fig. 10

Typical Thorium Deposit Produced in Mark VI Electrolytic
Cell