- CONFIDENTIAL -

RB 605

DEPARTMENT OF MINES

South Australia

RESEARCH AND DEVELOPMENT BRANCH

CHEMICAL RESEARCH SECTION

REPORT No. R.D. 60

"THE PRODUCTION OF URANIUM METAL BY ELECTROLYSIS IN MOLTEN CHLORIDES .. PART I"

by

R. G. Canning.

MICROFILMED

Copy No. 25

This document consists of 31 pages. DATE: May, 1957.

- CONFIDENTIAL -

40

CONTENTS

APPENDIX 1 - THERMOCHEMICAL CALCULATIONS.

CONTENTS (Continued)..

PAGE.

APPENDIX 1 - THERMOCHEMICAL CALCULATIONS (Continued)..

APPENDIX 2 - CONTROL OF CHLORINATION.

"THE PRODUCTION OF URANIUM METAL BY ELECTROLYSIS IN MOLTEN CHLORIDES"

PART I

by

R.G. Canning.

Abstract

A novel process for the manufacture of pure uranium metal is described, in which impure uranium oxides are converted to chlorides in a molten salt bath by means of a graphite chlorination reaction. The melt is then purified and uranium metal recovered as electrolytic powder.

The development of an analytical method for control of the chlorination reaction is outlined. Using this control, the feasibility of the chlorination and some factors affecting its efficiency are established. Work on the purification and metal recovery stages has not proved encouraging, and the only successful production of electrolytic metal was from a melt in which previously purified oxide had been used as feed material.

1. SUMMARY.

Preliminary investigation of a process for uranium metal manufacture is described. The main object of the work was to examine a new process put forward by A.R. Gibson of A.E.R.E., Harwell, and to test its possible application to South Australian raw materials.

Most of the investigations reported here were concerned with the conversion of impure uranium oxides to chlorides in molten salt baths by Gibson's graphite diffuser method. The feasibility of this procedure has been confirmed and some of the factors affecting the efficiency of chlorination have been examined. The development in these laboratories of a method for analytical control of the chlorination procedure was a major factor in the successful proving of this stage of the process.

Attempts to proceed with purification of the chloride melt and the electrolytic recovery of pure uranium metal have proved disappointing. Failures were apparently due mainly to the presence of oxysalts in the melts, one source of contamination being oxides in the crucible materials.

A reasonable yield of uranium metal powder was obtained from one test in which the process was modified to the extent that previously purified oxide was used as raw material. This eliminated the purification step. The uranium metal produced consisted of coarse dendritic powder and was not pyrophoric.

2. INTRODUCTION.

Following the visit of P. Dixon and the writer to the United Kingdom in 1954, considerable interest was shown in South Australia in a new process for uranium metal manufacture being developed by A.R. Gibson of A.E.R.E., Harwell. This process has been briefly described by Dixon (1955) and Canning (1955) and later amplified by Gibson and Buddery (1956). Further details have also been received in unpublished correspondence from Gibson.

It was considered that Gibson's process, although only in the early stages of laboratory development, showed promise of providing a cheaper route from impure uranium oxide to pure metal than the solvent extraction purification and the fluoride process at present used at the Springfields works of the U.K.A.E.A. The raw materials for Gibson's process would be more readily available in South Australia than those for the fluoride process, and the capital investment would probably be considerably less than the known investment at Springfields, as reported by Dixon (1955).

As South Australia was now producing uranium oxide at the Port Pirie Chemical Treatment Plant, it was logical to consider the possibility of this State developing a process to make pure uranium metal from local materials, with the aim of supplying the uranium fuel for possible future power reactors in this or other States of Australia. Such a process, to be within the financial capabilities of the State, would have to be considerably cheaper than the present Springfields process.

Preliminary investigations were therefore undertaken into Gibson's process, using South Australian uranium oxide as raw material. The process may be conveniently divided into the three stages, viz., chlorination, purification and metal recovery, and the experimental work has been grouped accordingly.

3. CHEMISTRY OF THE PROCESS.

The novel part of the process described by Gibson, is the conversion or chlorination stage. Uranium oxides are converted to chlorides in a molten salt bath by the combined action of chlorine gas and a reducing agent, such as sodium or barium sulphide, or graphite.

For sulphide chlorination Gibson suggests the following over-all reaction :

$$2UO_3 + 3Na_2S + 7Cl_2 \rightarrow 3SO_2 + 2UCl_4 + 6NaCl$$

Where an excess of sulphide is present :

$$2UCl_4 + Na_2S \rightarrow 2UCl_3 + 2NaCl + S$$

Gibson claimed that the absorption of chlorine was highly efficient and that the evolved gases consisted wholly of SO_2 and S provided a correct feed mixture of oxide and sulphide was maintained. Graphite chlorination was a later modification, and the reaction may be written :

$$UO_3 + 3C + 2Cl_2 \rightarrow UCl_4 + 3CO$$

This reaction has some advantage over the sulphide method in that the reducing agent does not consume chlorine. Graphite is also more readily obtained in a pure state than the anhydrous sulphides of sodium and barium.

It was suggested by Gibson that the chlorination procedure could be applied directly to impure uranium oxide. Iron oxide and other impurities would be converted to chlorides with the uranium. Metallic impurities less noble than uranium could then be precipitated from the melt by a controlled addition of calcium or magnesium metal. After pouring off the purified melt into a separate container, uranium could be precipitated in like manner and recovered as metal powder. Alternatively, the purification and uranium recovery could be carried out by electrolysis.

Thermochemical data and calculations, details of which are included in Appendix 1, indicated that chlorination should proceed readily at molten salt temperatures, and that higher temperatures should favour the reaction. Either calcium or magnesium metal could be used for precipitation of uranium and base metal impurities from chloride melts. Calculated decomposition potentials, shown in Appendix 1, indicated that it should be possible to separate iron and other impurities from uranium by controlled electrolysis of the molten chlorides.

4. RAW MATERIAL.

4.1 Crude Oxide

The impure uranium oxide used throughout these tests was produced from Radium Hill concentrate, during pilot scale tests of the process for the Port Pirie Chemical Treatment Plant. Several selected batches of crude oxide product were slurried with water and homogenised to provide one large batch of oxide. For convenience, this sample is referred to throughout as "crude oxide".

A complete analysis, chemical and spectrographic, of "crude oxide", as received, was carried out by the Analytical Section and is shown in Table 1. Table 2 lists the impurities, as elements, calculated as a ratio with respect to elemental uranium in the "crude oxide".

The uranium in "crude oxide" is largely in the form of calcium and magnesium di-uranates. The appearance of the oxide was not altered by ignition to 400°C.

TABLE 1.

COMPLETE ANALYSIS OF "CRUDE OXIDE"

Water	H_2O	9.38%		
Carbon di-oxide	CO_2	1.22		
Uranium tri-oxide	UO_3	70.96		
Ferric oxide	Fe_2O_3	5.32		
Aluminium oxide	Al_2O_3	0.03		
Titanium di-oxide	TiO_2	0.75		
Chromic oxide	Cr_2O_3	0.04		
Vanadium pentoxide	V_2O_5	0.04		
Thorium oxide	ThO_2	0.21		
Scandium oxide	Sc_2O_3	0.21		
Yttrium oxide	Y_2O_3	0.053		
Calcium oxide	CaO	3.96		
Magnesium oxide	MgO	3.69		
Sodium oxide	Na_2O	1.90		
Potassium oxide	K_2O	0.08		
Lithium oxide	Li_2O	2.5	p.p.m.	
Barium oxide	BaO	3	" " "	
Cupric oxide	CuO	0.01%		
Nickel oxide	NiO	0.025%		
Cobalt oxide	CoO	20	p.p.m.	
Lead oxide	PbO	0.18%		
Bismuth oxide	BiO	<10	p.p.m.	(N.D.)
Cadmium oxide	CdO	<3	" " "	(D.)
Zinc oxide	ZnO	<50	" " "	(N.D.)
Manganese oxide	MnO	0.04%		
Total lanthanon oxides	Ln_2O_3	0.27%		
Silica	SiO_2	1.20%		
Boric oxide	B_2O_3	60	p.p.m.	
Chlorine	Cl	0.03%		
Fluorine	F	0.02%		
Phosphorus pentoxide	P_2O_5	0.04%		
Sulphur tri-oxide	SO_3	0.42%		
Arsenic oxide	As_2O_3	<1	p.p.m.	(N.D.)
Antimony oxide	Sb_2O_3	<50	p.p.m.	(N.D.)
Molybdenum tri-oxide	MoO_3	<10	p.p.m.	(D.)
Tungstic oxide	WO_3	<75	p.p.m.	(N.D.)

Summation	100.09%	
Less oxygen	0.01	equivalent to Cl & F
Total ←	100.08%	

Individual Lanthanons.		p.p.m.
Lanthanum oxide	La_2O_3	1500
Cerium oxide	Ce_2O_3	500
Praseodymium oxide	Pr_2O_3	30
Neodymium oxide	Nd_2O_3	70
Samarium oxide	Sm_2O_3	15
Europium oxide	Eu_2O_3	0.7
Gadolinium oxide	Gd_2O_3	25
Terbium oxide	Tb_2O_3	17
Dysprosium oxide	Dy_2O_3	65
Holmium oxide	Ho_2O_3	55
Erbium oxide	Er_2O_3	150
Thulium oxide	Tm_2O_3	130
Ytterbium oxide	Yb_2O_3	150
Lutecium oxide	Lu_2O_3	17

TABLE 2.

IMPURITIES IN "CRUDE OXIDE" CALCULATED AS ELEMENTS "WITH RESPECT TO" ELEMENTAL URANIUM.

Element	Percentage w.r.t. uranium		
Fe	6.30		
Al	0.027		
Ti	0.76		
Cr	0.046		
V	0.037		
Th	0.31		
Sc	0.23		
Y	0.071		
Ca	4.79		
Mg	3.77		
Na	2.39		
K	0.11		
Li	2	p.p.m.	
Ba	4.6	" " "	
Cu	0.014%		
Ni	0.034%		
Co	27	p.p.m.	
Pb	0.29%		
Bi	<15	p.p.m.	(N.D.)
Cd	< 5	" " "	(D.)
Zn	<70	" " "	
Mn	0.05%		
Total lanthanons	0.40%		
Si	0.95%		
B	31	p.p.m.	
Cl	0.05%		
F	0.03		
P	0.03		
S	0.29		
As	< 1	p.p.m.	(N.D.)
Sb	< 70	" " "	(N.D.)
Mo	< 11	" " "	(D.)
W	<100	" " "	(N.D.)

Individual Lanthanons.	p.p.m.
La	2,200
Ce	720
Pr	44
Nd	100
Sm	22
Eu	1
Gd	36
Tb	25
Dy	95
Ho	81
Er	220
Tm	195
Yb	220
Lu	25

D. = detected.
N.D. = not detected.

4.2 Pure Oxide

Nitrate solutions of crude oxide or of recovery precipitates were purified by a large scale cellulose column procedure similar to that used for analytical purposes.

Pure uranium oxide was recovered from the nitrate solutions by precipitation with ammonia, the filtered precipitate being dried and ignited to 400°C. to give high purity UO_3.

5. EQUIPMENT.

5.1 Furnace

Figure 1 shows diagrammatically the 2 kilowatt furnace which was constructed for initial work. Crucible temperatures up to 800°C could be readily maintained, although the massive nature of the furnace construction caused a slow heating rate.

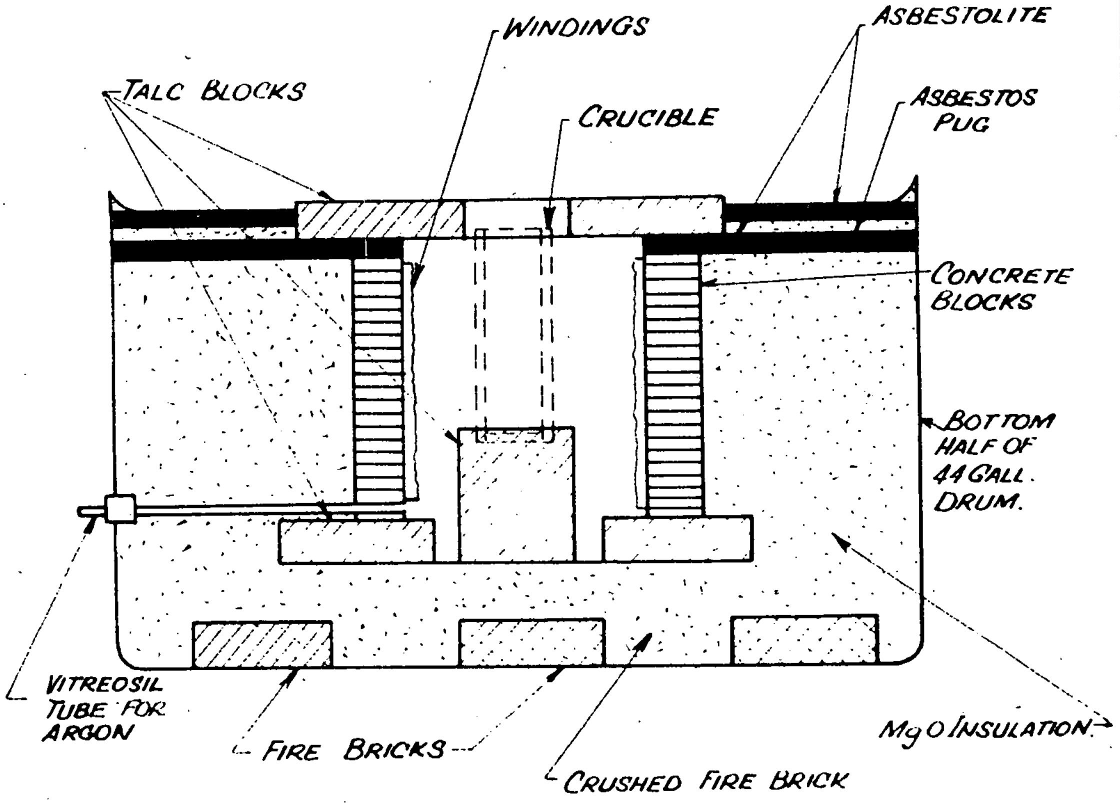
5.2 Crucibles

Crucibles were machined from 4 inch rods of electrode graphite (National Carbon), with wall thickness 0.5 inches and depth up to 12 inches. For later stages of the work, 4 inch diameter billets of EYX 24 grade (Morgan Crucible Co.) graphite were used. Other materials tested for use as crucibles included vitreosil and thermal mullite (Thermal Syndicate Ltd.), alutite, carbolox and mullox (Non-porite Ltd.), re-crystallised alumina and brown mullite (Morgan Crucible Co.), moulded and massive steatite from Mt. Fitton, South Australia, and plumbago (metallurgical graphite/clay).

With the exception of graphite, all of these materials were found to be too porous, too fragile, subject to attack by molten chlorides, or not sufficiently resistant to thermal shock. Although graphite was somewhat porous, it had the advantage of being easily worked and proved to be the most useful material.

In an attempt to render the graphite less porous, several new and used crucibles were treated with molten pitch for an extended period. The bulk of the pitch was then poured

FIGURE.-1.



ELECTRIC FURNACE

R.S. 249.

out of the crucible and the remainder carbonised by heating in an argon atmosphere to 800°C. The crucibles were encased in outer steel containers during this treatment. For some tests, untreated graphite crucibles were used in similar steel containers.

Crucible lids were cut from graphite or from massive steatite. The latter proved very satisfactory, being easily cut and drilled in its natural state, but becoming quite hard after use at high temperatures.

5.3 Stirrer

An all-graphite stirrer (Fig. 2) was made from a roughly shaped propellor screwed on to a threaded graphite rod. A short adaptor was machined from brass rod to fit the chuck of the stirrer motor, and was drilled and tapped to screw over the threaded end of the graphite shaft.

5.4 Diffuser block

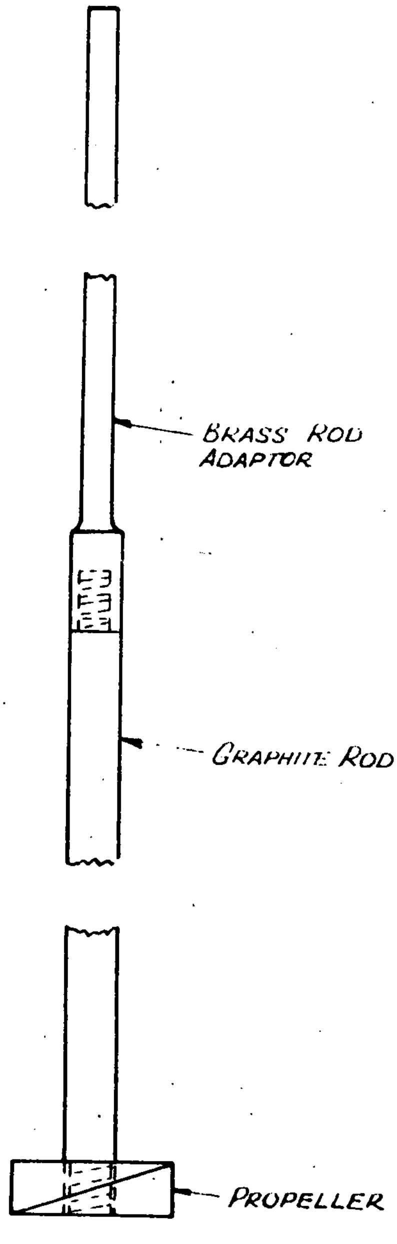
This was cut from graphite rod, patterned on a small model forwarded by A.R. Gibson from A.E.R.E., Harwell (Fig. 3).

Standard dimensions were 2.75 inches diameter, 2.5 inches high, with 16 chlorine channels. A central tube of vitreosil served as chlorine feed-tube.

5.5 Electrodes

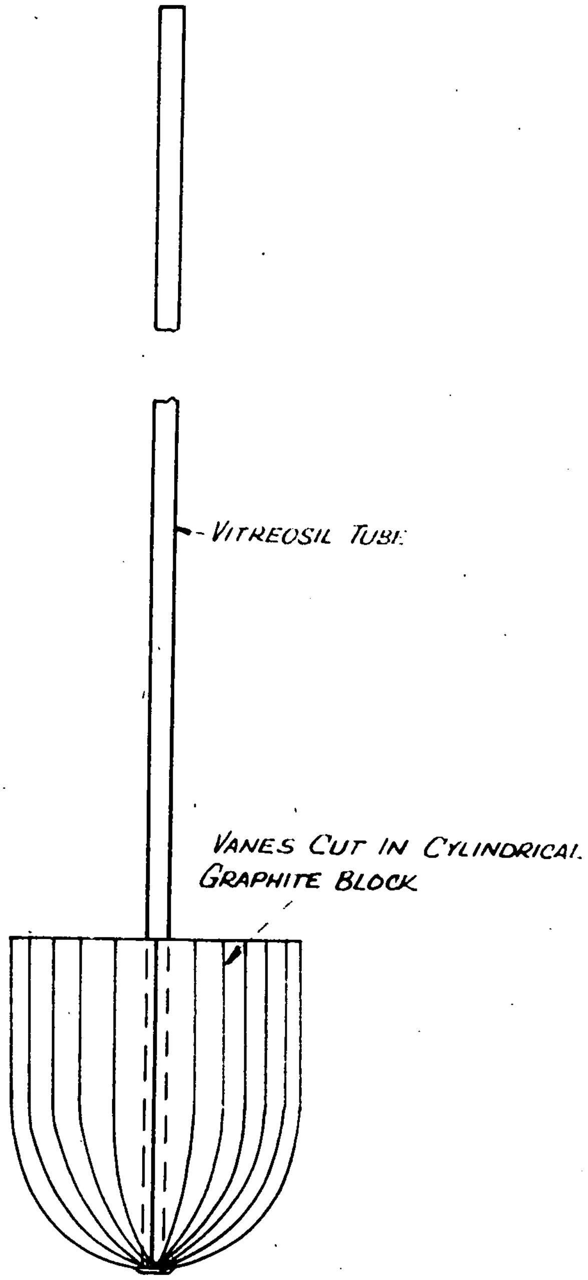
The graphite crucibles were generally used as anodes, a graphite connecting rod being tapped into the rim of the crucible. In non-conducting crucibles, graphite spade anodes (Fig. 4) were used, and in the tests where hydrogen was used for reduction, a combined anode/gas distributor (Fig. 5) cut from graphite, was employed.

Cathodes were of pure molybdenum in strip form. It was found necessary to protect the molybdenum against attack by HCl gas when hydrogen was being used to keep the melt reduced during electrolysis. A mullite tube, sheathing the cathode to within 1 inch of the melt surface, served this purpose, a down-draught of argon being maintained through the mullite tube.



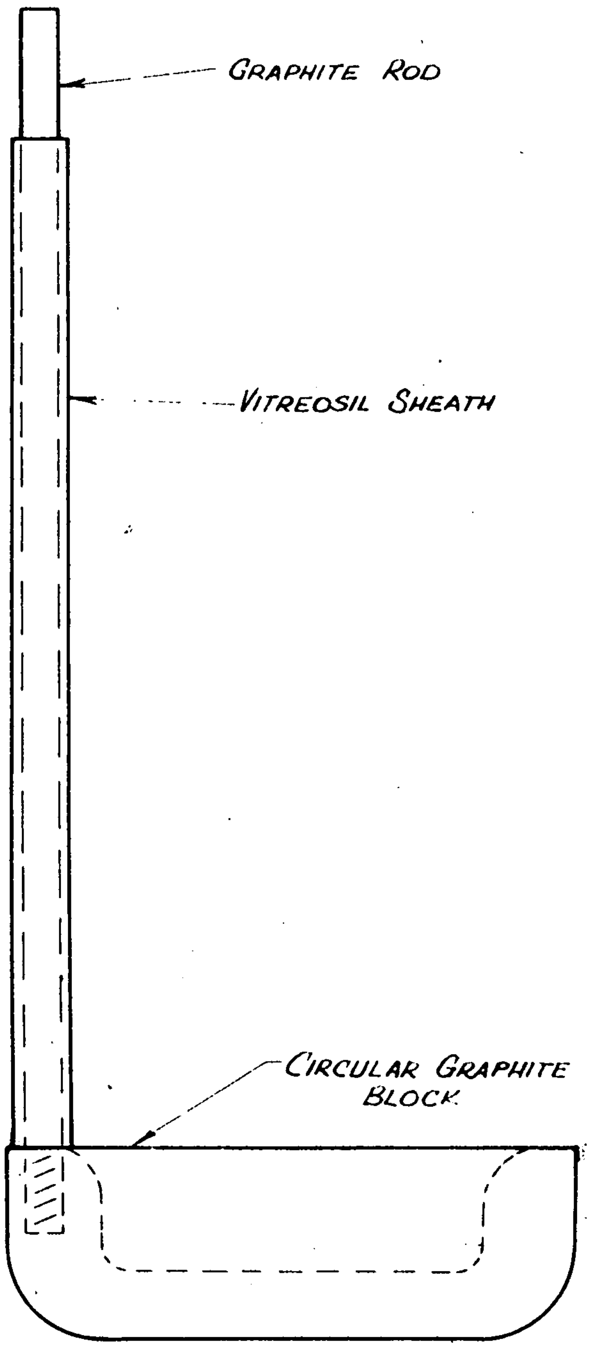
STIRRER

FIGURE.-2.



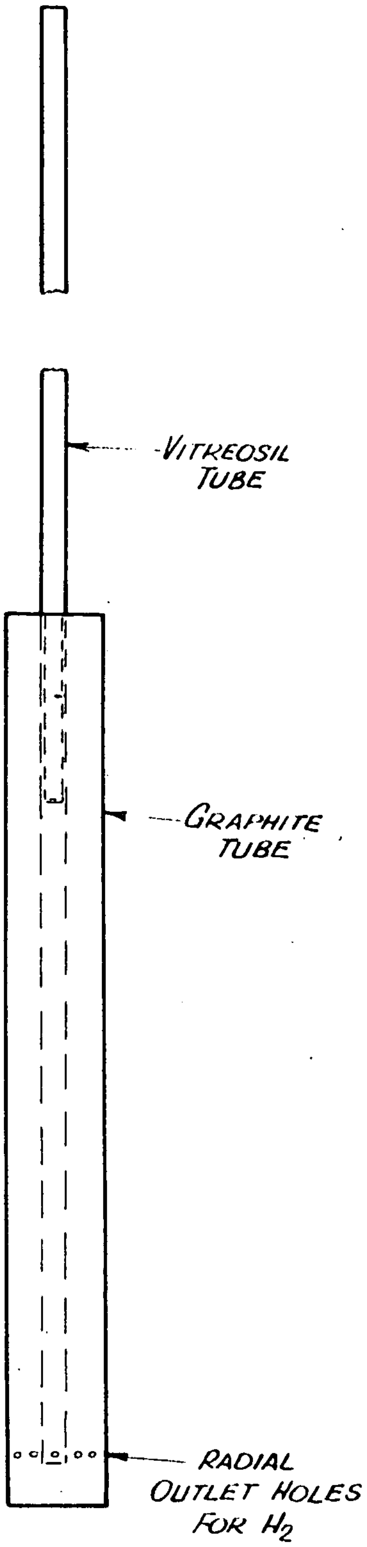
DIFFUSER

FIGURE.-3.



SPADE ANODE

FIGURE: 4.



ANODE / HYDROGEN DISTRIBUTOR.

FIGURE: 5.

Alundum crucibles, supported from the cathode itself (Fig. 6), were used as collecting pots for non-adherent cathode deposits.

For electrolytic purification tests, iron rod cathodes, protected against HCl corrosion, were used.

5.6 Gas Flow Meters

Flow meters of the type shown in Fig. 7 were constructed and calibrated for chlorine, hydrogen and argon.

5.7 Pyrometer

A chromel-alumel type thermocouple in a vitreosil sheath was used for temperature measurement.

5.8 Analyses of Graphite

Three samples of graphite used for this work were submitted to the Analytical Section for total ash determination and spectrographic analysis of the ash. Table 3 shows the total ash and bulk density figures for each sample.

TABLE 3.

GRAPHITE ANALYSES

		O'Brien's electrode graphite (National Carbon)	Morgan's EYX24 grade	
			old stock	new stock
Bulk density (S.G.)	-	1.66	1.67	1.72
Total ash content	-	0.21%	0.33%	0.62%

Major impurities in the ash were :- calcium, silicon, aluminium and titanium.

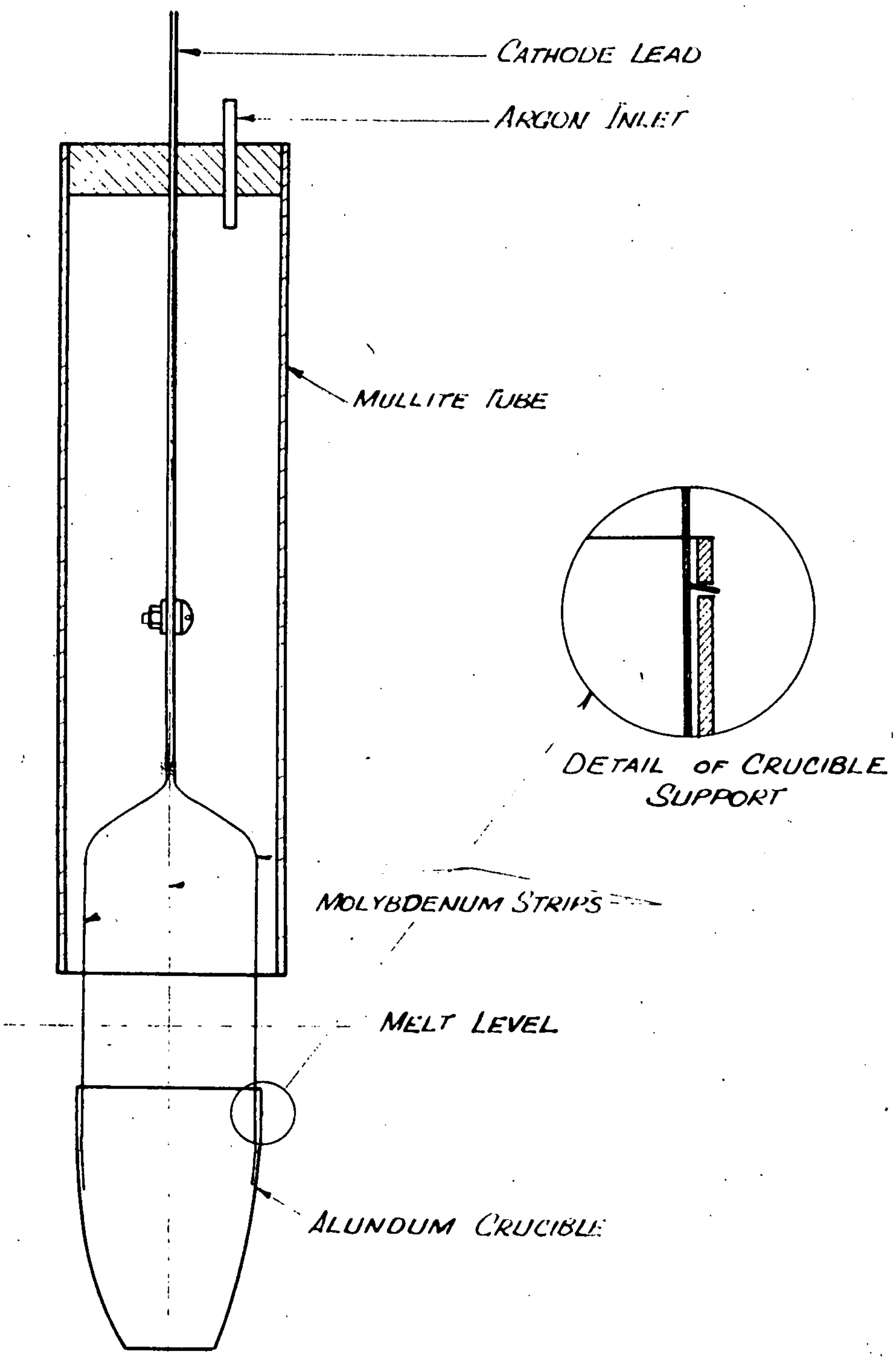
Minor impurities were:- vanadium, chromium, manganese and magnesium.

Other elements were in insignificant amounts.

6. ANCILLARY MATERIALS.

6.1 Salts

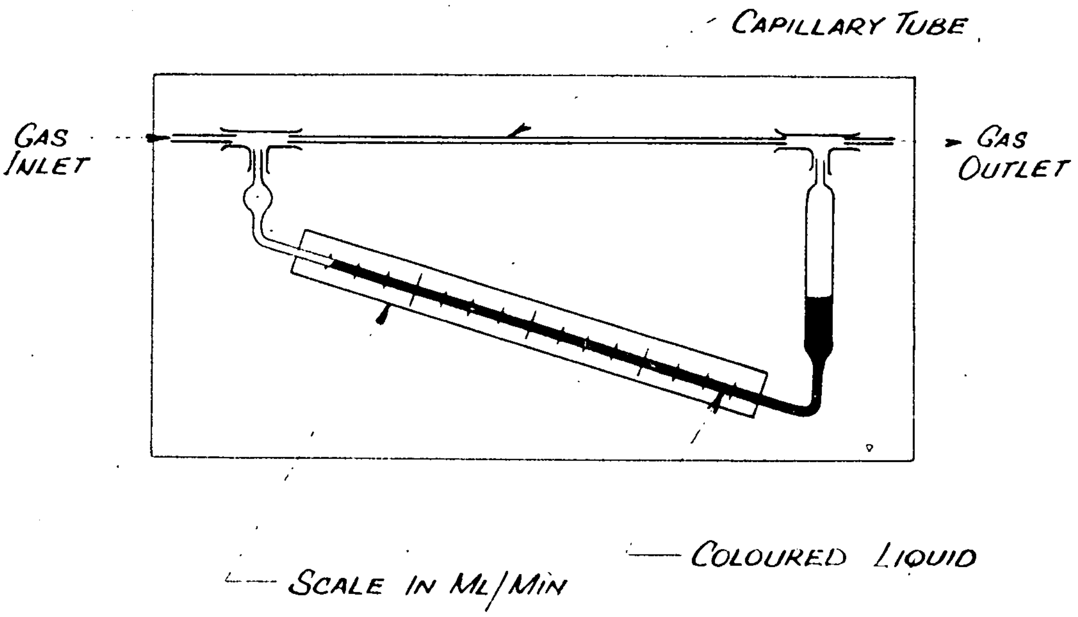
A.R. anhydrous NaCl and KCl were used throughout for the initial molten salt pools.



CATHODE ASSEMBLY

FIGURE.– 6.

FIGURE – 7.



GAS FLOW METER.

R.S. 253.

6.2 Sulphides

Sodium sulphide was available only in the hydrated form ($Na_2S.\ 9H_2O$). After drying at the temperature necessary to remove most of the water and re-grinding to a powder, considerable NaOH was present. Anhydrous barium sulphide (commercial) was available but analyses showed this to contain only 80% BaS. A major impurity was $BaSO_4$ (5% of total).

6.3 Magnesium metal

Chips of magnesium were milled from billets of pure metal. These were thicker and larger than the "turnings" available as A.R. Grignard reagent. The latter "turnings" were also used successfully, although it was considered desirable to use larger chips.

6.4 Gases

Pure chlorine, hydrogen and argon were obtainable in cylinders. All gases were dehydrated by passing through silica gel.

7. EXPERIMENTAL PROCEDURE.

7.1 Chlorination

7.1.1 General technique :

Operating techniques were continually altered as better methods were evolved. Several conditions were shown to be essential, such as the complete exclusion from the melt of air and moisture in any form, in order to prevent hydrolysis and oxidation with the formation of oxysalts.

To exclude air, lids of graphite and later, steatite were fitted to the crucibles. These lids were perforated with suitable holes for stirrer shaft, chlorine feed-tube, argon feed tube, electrodes and thermocouple. Argon was streamed into the crucible above the melt at flow-rates of 100 to 400 ml/minute during and after chlorination.

7.1.2 Sulphide method :

A molten pool of mixed salts (NaCl and KCl) was first formed in the crucible at the required temperature, normally

700°C to 800°C. The melt was stirred continuously while chlorine was bubbled in through a straight vitreosil tube at the desired flow-rate. The feed mixture of oxide and sulphide in appropriate proportions (30% excess sulphide over theoretical) was added manually in small portions over a period of up to two hours.

7.1.3 Graphite diffuser method :

After melting the initial pool of mixed salts, chlorine was introduced through a graphite block diffuser (Fig. 3), at the desired flow-rate. The oxide feed material, previously ignited to 400°C, was fed into the melt in small portions over a period of 0.5 to 2 hours, commencing at the same time as the chlorine. The oxide may be fed in as rapidly as possible without building up a solid deposit in the bottom of the melt thus limiting circulation. Ideally, all the oxide should remain suspended in the molten salts, the circulation being maintained by the chlorine gas bubbling up around the diffuser block. It was found impracticable to fit a stirrer into the melt.

It was shown that under suitable conditions the chlorine could be absorbed with high efficiency, the uranium oxide first being converted to soluble oxy-chloride (UO_2Cl_2) giving a yellow melt, then further reduced and chlorinated to the green tetrachloride (UCl_4). When crude oxide was used as feed material, thick white fumes from evolved titanium tetrachloride ($TiCl_4$) appeared at an intermediate stage of the conversion. Red-brown fumes of ferric chloride ($FeCl_3$) were produced from the melt eventually, this being taken as a guide to the end of the reaction.

7.1.4 Control of Chlorination :

It was considered essential that some reliable method of determining the progress and the completion of chlorination be found. Gibson had apparently relied upon such indications as the evolution of ferric chloride fumes and on the appearance of samples withdrawn from the melt.

After some investigations along different lines, an analytical method for determining the degree of chlorination of uranium in a sample was developed. This method and the investigations leading to its adoption are detailed in Appendix 2. Chlorination efficiencies quoted in this report have been determined by this means.

Samples were withdrawn from the melts by means of vitreosil dip tubes, and run into warm, dry vitreosil crucibles. After rapid cooling the samples were easily loosened from the crucibles.

7.1.5 Systematic examination of chlorination :

Owing to the difficulty of obtaining sulphides pure and anhydrous, it was decided to limit systematic investigations to the graphite diffuser method of chlorination. A major advantage of this method was that the carbon and the chlorine would not react together wastefully and non-effectively as was the case with sulphides and chlorine.

Factors affecting the efficiency of chlorination, such as temperature, chlorine flow-rate and total uranium concentration, were examined in a series of controlled chlorination tests using crude oxide as feed material.

7.2 Reduction and Purification

7.2.1 By magnesium metal :

The general procedure adopted was to introduce a thoroughly dried, pre-heated graphite stirrer into the fully chlorinated melt. Magnesium metal, slightly in excess of the calculated quantity, was fed slowly into the stirred melt during a period of 30 minutes to 1 hour. After further stirring for 15 to 30 minutes to allow completion of reaction, the precipitate was allowed to settle for 10 minutes. Precipitations were carried out at 700°C with a 300 to 400 ml/min. stream of argon over the melt.

In some early tests, before development of analytical control, the clear supernatant melt, supposedly free from iron and other base metal impurities, was decanted into a clean pre-heated crucible. There was no tendency for the precipitate to pour out with the clear melt. A practical difficulty associated with pouring arose from the deposit of ferric chloride and other volatile chlorides around the rim of the crucible. These contaminated the purified melt. Also, it was found practically impossible to exclude air from contact with the melt during pouring, although streams of argon were directed over the melt surface and into the receiver crucible.

In a series of purification tests carried out after analytical control was developed, the required amount of magnesium metal was calculated from the analysis of the fully chlorinated melt and the estimated total weight of salts. Sufficient magnesium metal was added to reduce iron and other base-metal impurities to metal, to reduce all tetravalent and pentavalent uranium to the trivalent state and in addition to precipitate several grams of uranium metal. Samples taken before and after precipitation were analysed in the usual manner. In one of these tests, magnesium metal was added in stages. Time for completion of reaction and for the settling of the precipitate was allowed and a sample of the clear melt was taken after each stage. No pouring was attempted.

7.2.2 By hydrogen reduction and electrolysis :

After completion of chlorination, hydrogen was bubbled into the melt for 1 to 2 hours, and then continued throughout the electrolysis at flow-rates up to 600 ml/min. An iron rod cathode was used, protected against HCl corrosion above the melt by a mullite sheath, which was also used as an inlet for argon. The hydrogen was bubbled in through a graphite distributor/anode (Fig. 5), in order to introduce the hydrogen into the melt in the region where anodic chlorine would be liberated. Trouble was experienced with blockages in the distributor and it was doubtful whether the melts treated in this way were fully reduced.

7.3 Recovery of Uranium

Metal was recovered by the electro-refining procedure, namely, precipitation of uranium onto the floor of a graphite crucible by magnesium metal addition, followed by electrolysis on to a molybdenum cathode, using the graphite crucible (i.e. the precipitated uranium) as anode.

Metal recovery by electro-winning (i.e. direct electrolysis), using hydrogen gas to keep the melt reduced to the UCl_3 state, was not attempted because of difficulties in the preceding electrolytic purification stage.

8. EXPERIMENTAL RESULTS.

8.1 Chlorination

Table 4 summarises the results of investigations into factors affecting the efficiency of chlorination of crude oxide. Efficiency is expressed as the percentage chlorination of uranium oxide achieved after the total theoretical quantity of chlorine had been passed into the melt. The tests were carried out in graphite crucibles 3" internal diameter, 8 inches depth, and 0.5 inches wall thickness. The diffuser block was 2.5 inches high and 2.75 inches diameter, fluted with sixteen channels. The total melt was approximately 700 g. in each case.

TABLE 4.
SUMMARY OF CHLORINATION TESTS.

Test No.	Uranium Concentration in final melt %	Temperature °C.	Cl_2 Flow-rate ml/min/% U	Efficiency %
18	9	700	20	55
19	9	"	30	46
26	9	"	40	40
20	20	"	14	71
21	20	"	21	74
23	30	"	9	82
22	30	"	12	87
24	30	"	15	83
25	30	800	15	93

Graphs illustrating the rate of chlorination of uranium in each of these tests are shown in Figs. 8 to 11 inclusive.

FIGURE. 8.

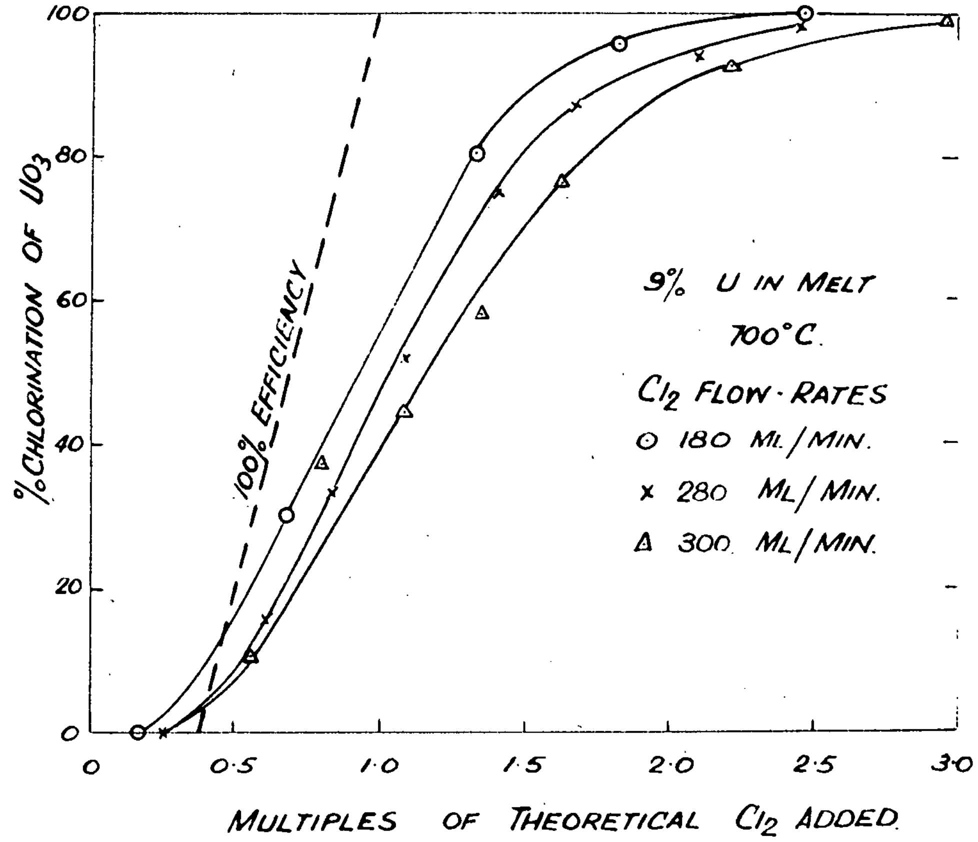
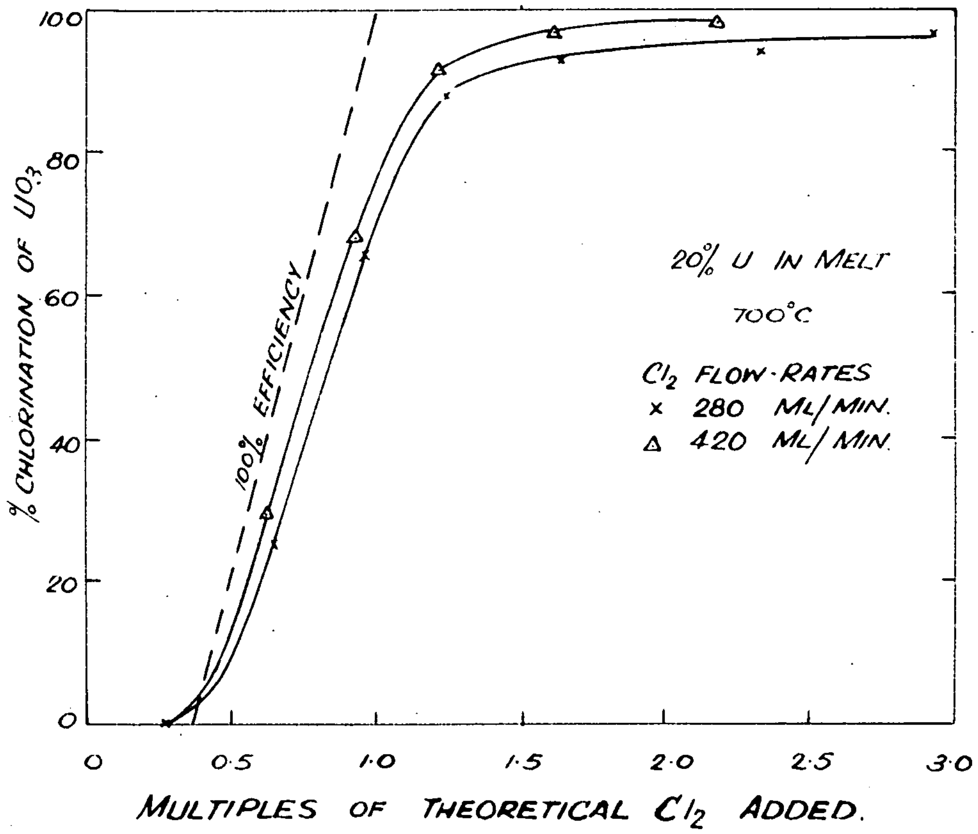


FIGURE. 9.



CHLORINATION OF CRUDE OXIDE

FIGURE. 10.

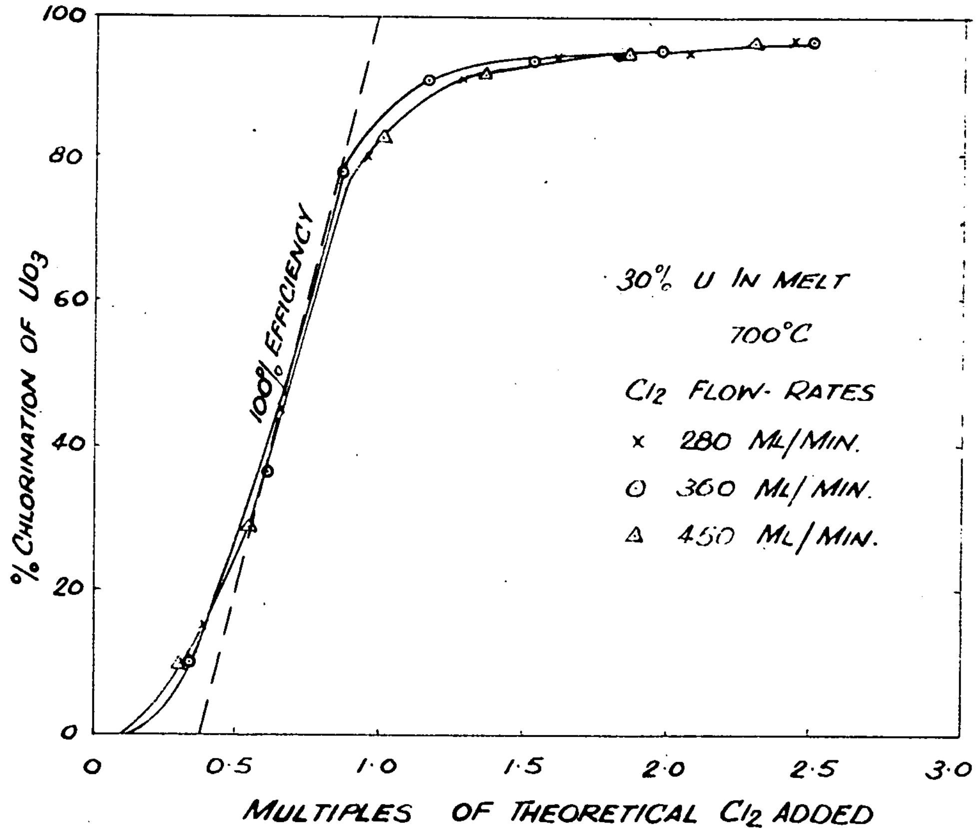
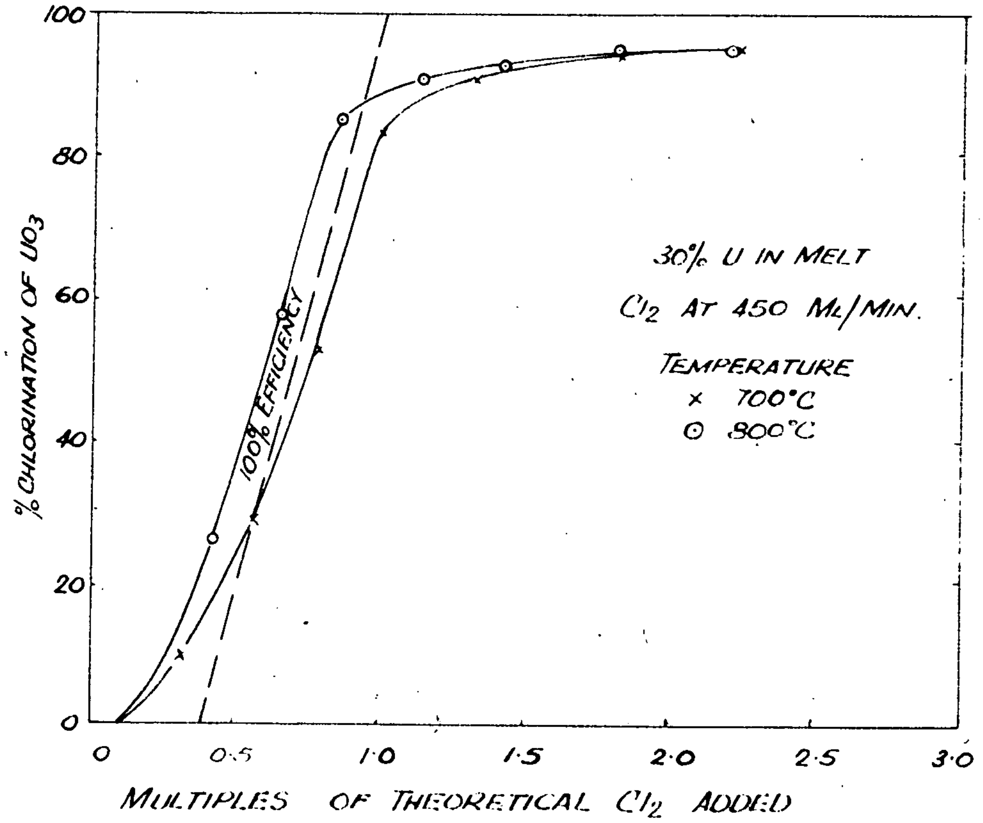


FIGURE. 11.



CHLORINATION OF CRUDE OXIDE

Calculations based on the complete analysis of the crude oxide showed that 40 percent of the total theoretical chlorine requirement would be consumed by the impurities, and it was assumed that most of these impurities would be chlorinated before uranium. In figs. 8 to 11, the line representing 100 percent efficient use of chlorine with respect to uranium was therefore drawn from zero chlorination at 0.4 theoretical chlorine to 100 percent at 1.0 theoretical chlorine.

8.2 Reduction and Purification

8.2.1 By Magnesium metal :

During early work on the process, eight melts were treated by this means. Complete precipitation of iron was achieved in four instances, but larger amounts of uranium than were anticipated were co-precipitated.

The results of later, controlled tests are given in Tables 5 and 6. In test run No. 26, carried out in a pitch-treated graphite crucible, the magnesium metal was added in stages. The analysis of the clear melt at each stage is shown in Table 5. The melt had been fully chlorinated on the previous day, but had apparently been contaminated with oxygen during over-night storage at 110°C and re-melting preparatory to reduction. The first sample was taken immediately prior to magnesium addition.

TABLE 5.
PURIFICATION TEST - Run No. 26.

Sample No.	1	2	3	4	5
Stage of precip. g. Mg added	Nil	5.5 g. (theoretical)	6.5 g	7.5 g	melt held for 1 hr.
Melt analysis					
U content %	10.3	7.5	7.0	6.6	4.5
Fe content %	0.57	0.32	0.29	0.55	0.50
Degree of chlorination %	91	93	71	50	28
Valence of U	4.3	4.0	4.8	5.1	5.8

Table 6 summarises the conditions and final results of the above and two other purification tests and includes all information considered to be relevant to the contamination of the melts with oxygen and other impurities.

TABLE 6.

SUMMARY OF PURIFICATION BY Mg PRECIPITATION.

Test No.	26	27	28
Crucible	pitch-treated graphite	same crucible * as 26	new graphite
Previous use of crucible	one chlorination	(two chlorinations (and one Mg (precipitation	one chlorination
Treatment of melt after chlorination	stored overnight at 110°C	held molten overnight under argon	no delay.
Total Mg added (excess over theoretical)	35% excess	2% excess	35% excess
Analysis of melt before precipitation.			
U content	10.3%	19.3%	19.0%
Fe content	0.57%	1.06%	0.43%
Degree of chlorination	91%	98%	100%
Analysis of melt after precipitation.			
U content	6.6%	18.4%	11.5%
Fe content	0.55%	$<$ 0.03%	0.40%
Degree of chlorination	50%	approx. 100%	85%
Condition of crucible	Sound	Leaking rapidly by end of precip.	Sound
Comments.	Melt was attacking oxide in ash of pitch and graphite. UO_2 precipitated in preference to Fe.	Successful precip. of Fe, due to all oxides having been leached from graphite previously. Crucible so porous that most of melt leaked away.	Oxides in ash of new graphite being attacked rapidly enough to cause UO_2 precipitation in preference to Fe.

* The crucible was shown to be free of oxide impurities by successfully holding a fully chlorinated melt overnight at molten temperature.

8.2.2 By hydrogen reduction and electrolysis :

In first attempts to remove impurities by electrolysis, using hydrogen gas to prevent anodic oxidation, the Fe & Mo cathodes were corroded by the evolved HCl gas. This was overcome by protecting the cathodes as described previously. No corrosion was found on the immersed portion of the cathodes.

Further attempts to purify melts by this procedure failed to reduce the Fe content of the melts sufficiently, and in each case the cathode product was found to be mainly UO_2.

One of these tests was carried out in a vitreosil container and it was afterwards established that sufficient excess chlorine (by comparison with later controlled tests) had been used to chlorinate the melt fully. Despite this, large quantities of UO_2 were deposited on the cathode, from which it was inferred that the melt was attacking the vitreosil and taking up oxygen while liberating silicon tetrachloride.

8.3 Recovery of uranium metal

The only successful production of metal to date was from a test using previously purified oxide as raw material, which enabled the purification stage to be eliminated. A small quantity (15 g.) of coarse dendritic metal powder (S.G. = 18.6) was recovered by the electro-refining procedure at a current efficiency of 25 percent. The metal powder was not pyrophoric, but could be ignited readily to burn fiercely in air. A typical vigorous reaction with concentrated HCl was also noted.

Certain cathode products produced from purified melts which had been poured into a second crucible contained enough fine metal powder to give the metal reaction with HCl, but these products were grossly contaminated with oxide and carbide. No analyses were considered to be warranted.

9. DISCUSSION.

9.1 Materials of construction

Despite the loss of salts through porous graphite crucibles, it was clear that this material was the most suitable one for containing molten chlorides. The use of graphite crucibles set in an outer steel shell partly overcame the difficulty of porosity but the use of such a crucible as anode during electro-refining was likely to contaminate the melt with iron dissolved anodically from the steel and diffused through the graphite. Contamination from the steel by diffusion occurred during chlorination in at least one case. Attempts to densify the graphite with pitch only provided more contaminating oxide material from the ash of the pitch. Better grades of graphite with higher density and lower ash content are desirable. For work on a larger scale it should be possible to use a graphite lined steel container with the melt heated internally. The outer shell of the container could be cooled sufficiently to cause a crust of solid salt to form inside the porous graphite. This crust would serve as the container for the melt.

The main objection to vitreosil containers was the tendency to crack if any salts were allowed to cool in the crucible. It was also evident that vitreosil was attacked by molten chlorides resulting in oxygen being taken up by the melt.

9.2 Chlorination

The development of an analytical method for the determination of oxygen associated with uranium in the melt enabled the chlorination procedure to be controlled and the factors affecting it examined. Chlorination by the graphite diffuser method has been proved feasible and controllable.

Efficiency of chlorination was greater at higher concentrations of uranium in the melt, and was improved at higher temperatures as indicated by thermochemical calculations. The different chlorine flow-rates used did not significantly affect efficiency, except possibly at a uranium concentration of 9 percent. With a concentration of 30 percent uranium and a temperature of 800°C, 93 percent chlorination was reached after passing the theoretical quantity of chlorine, and a 50 percent excess of chlorine was ample to ensure maximum chlorination. The sulphide method of chlorination was not considered worthy of further investigations after the first preliminary tests which were not promising. It was also considered that the impure nature of the anhydrous sulphides available would prevent complete removal of oxygen from the chlorinated melt.

9.3 Purification and Recovery of Uranium

It was evident from the results shown in Tables 5 and 6 that failure to achieve purification was caused mainly by contamination of the melt with oxygen from oxide impurities in the graphite crucibles and in the ash of the pitch used for treating the graphite. Similar take-up of oxygen was noticed earlier from a vitreosil crucible. The final result was that uranium was preferentially precipitated as UO_2, leaving iron and other impurities in the melt. For satisfactory separation of impurities, the melt should not only be chlorinated until free of oxy-salts, but also should not come into contact with any oxide material preparatory to and during reduction.

Test No. 27 (Table 6) showed that it was possible to bring a graphite crucible to the state where no further oxygen contamination of the melt was taking place. Under these conditions, successful separation of impurities was achieved with only a very small excess over the theoretical amount of magnesium metal, and only a small amount of uranium co-precipitated. Unfortunately, by the time the graphite had been brought to this state of purity it was apparently so porous that rapid leakage of salts occurred.

Although the impurities could be precipitated successfully, the purified melt, if decanted from the crucible, could be re-contaminated in several ways. Contamination could result from the presence of ferric chloride and other volatile chlorides on or near the rim of the chlorination crucible. There was no doubt that the reduced and purified melts (containing UCl_3) rapidly took up oxygen when exposed to air, and this seemed unavoidable in the pouring operation. Katz and Rabinowitch (1951) reported that UCl_3 at 700°C rapidly oxidises to UO_2Cl_2 in air. Oxide impurities in the graphite of the receiving crucible also caused oxygen contamination of the purified melt, the final result being that uranium oxide, rather than metal, deposited on the cathode during electrolysis.

It was considered significant that the only reasonably successful production of metal was from a melt which had not been poured into a second crucible. The products electrolysed from purified melts which had been poured were grossly contaminated with oxide.

The alternative procedure for purification by electrolysis, using hydrogen injection to keep the melt reduced, did not show any promise of success. Similar difficulties from oxygen contamination caused preferential deposition of UO_2. Apart from this consideration, it was doubtful whether a clear-cut removal of impurities could be obtained electrolytically, even in the absence of oxysalts, without the wasteful co-deposition of a large proportion of the uranium.

10. GENERAL DISCUSSION OF THE GIBSON PROCESS.

Although the feasibility and the efficiency of the conversion of uranium oxides to chlorides in a molten salt bath has been confirmed, the difficulties associated with the purification stage of the process have prevented a complete study being made, in that no metal has been produced directly from South Australian uranium oxide.

Laboratory scale work on the latter stages of the process has not been encouraging, and it is considered that the process may prove to be unworkable in the form outlined by Gibson. However, it is possible that many of the troubles experienced so far may be less evident on a larger scale. This is most likely to be the case with regard to oxygen contamination of fully chlorinated and purified melts. It may also be possible to modify the process in some way to reduce the purification difficulties and further investigations will be directed towards this end.

If a purer, less porous grade of graphite cannot be obtained, the use of outer steel containers for graphite crucibles will be continued. This should prevent undue loss of salts through leakage, but at the risk of iron contamination by diffusion through the graphite. The complete process should be carried out as rapidly as possible, in order to cut down the time during which the melt may absorb contaminating oxides.

The final test of the process must be the purity of metal produced, and it is hoped that further work will enable the production of sufficient metal to allow complete spectrographic analyses to be made.

11. REFERENCES.

Canning, R.G. (1955). Report on Overseas Visit of 1954. (Departmental report).

Dixon, P. (1955). Report on Overseas Visit of 1954. (Departmental report).

Gibson, A.R. & Buddery, J.H. (1956). An oxide-chloride conversion process for the extraction of certain metals. (Inst. Min. & Met. - Symposium on the Extraction Metallurgy of some of the less common metals, 22nd & 23rd March, 1956).

Katz and Rabinowitch (1951). The Chemistry of Uranium. Part I. p. 459. (McGraw-Hill Book Co.)

APPENDIX 1.

THERMOCHEMICAL CALCULATIONS.

1. CHLORINATION REACTION.

The free energies of reaction for some of the possible chlorination equations have been calculated from data taken from Katz and Rabinowitch (1951) and Kubaschewski and Evans (1951). Although it was shown during experimental work that the graphite diffuser type of chlorination proceeded via intermediate oxy-chlorides (UO_2Cl_2 and $UOCl_2$), no data were available for these compounds, hence calculations were made only for the over-all reactions. It was realised that some intermediate step might prove to be a controlling factor. The free energies shown in Table 7 indicated that chlorination should proceed readily at molten salt temperatures, and that higher temperatures would favour the reaction.

As no detailed investigations were planned for the sulphide type chlorination, no calculations for these reactions were made. In addition, insufficient data on sulphides were available to enable these to be made with certainty.

TABLE 7.

FREE ENERGIES OF CHLORINATION REACTIONS.

Reaction	Free energy of reaction (Kilocalories)		
	900°K (627° C.)	1,000°K (727° C.)	1,100°K (827° C.)
$UO_2 + 2C + \frac{3}{2} Cl_2 \rightarrow UCl_3 + 2CO$	- 39.3	- 42.5	- 45.8
$UO_3 + 3C + \frac{3}{2} Cl_2 \rightarrow UCl_3 + 3CO$	- 67.0	- 74.4	- 81.8
$UO_2 + 2C + 2Cl_2 \rightarrow UCl_4 + 2CO$	- 62.8	- 64.6	- 66.4
$UO_3 + 3C + 2Cl_2 \rightarrow UCl_4 + 3CO$	- 90.1	- 95.9	- 101.8

2. REDUCTION AND PRECIPITATION.

The successful precipitation of impurities and of uranium by means of calcium or magnesium metal depends on their relative positions in the electrochemical series for molten chlorides. This differs from the series for aqueous solutions.

Such a series has been given by Kortum and Bockris (1951) which is shown below. Delimarskii (1955) has determined the electrode potentials of a series of metals in their molten chlorides, taking a sodium electrode in its pure salt as zero potential. This series is compared with that of Kortum and Bockris in Table 8.

TABLE 8.

ELECTROCHEMICAL SERIES IN MOLTEN CHLORIDES.

Kortum & Bockris (1951)	Delimarskii (1955)	
Electrochemical series	Electrodes	Potentials at 700°C.
	Na/Na^+	0.00
	Ca/Ca^{++}	+ 0.01
	Mg/Mg^{++}	+ 0.78
	Mn/Mn^{++}	+ 1.51
Al	Al/Al^{+++}	+ 1.78
Zn	Zn/Zn^{++}	+ 1.96
Cd	Cd/Cd^{++}	+ 2.11
Pb	Pb/Pb^{++}	+ 2.27
Fe	Sn/Sn^{++}	+ 2.31
Cu	Fe/Fe^{++}	+ 2.33 (at m. pt)
Ag	Ni/Ni^{++}	+ 2.36
Sn	Co/Co^{++}	+ 2.42
Co	Hg/Hg^{++}	+ 2.53
Ni	Ag/Ag^+	+ 2.55
Hg	Cu/Cu^+	+ 2.65
Sb	Bi/Bi^{+++}	+ 2.75
Bi	Sb/Sb^{+++}	+ 2.90

Uranium, vanadium, titanium, and thorium are not included in the above series, but their relative positions may be gauged by a comparison of the decomposition potentials of chlorides at 800°C., calculated from free energies of formation. Table 9 lists calculated decomposition potentials, the data being derived from various sources.

TABLE 9.

DECOMPOSITION POTENTIALS OF MOLTEN CHLORIDES AT 800°C.

Salt	e.m.f.
NaCl	3.3 V
$CaCl_2$	3.3
$MgCl_2$	2.5
UCl_3	2.4
$ThCl_4$	2.4
$ZrCl_2$	2.4
$AlCl_3$	1.9
VCl_2	1.7
$TiCl_2$	1.65
$FeCl_2$	1.2

From the above tables it can be seen that all the metals below magnesium in the series quoted by Delimarskii, and vanadium and titanium in addition, should be readily separable from uranium either by magnesium metal precipitation or by controlled electrolysis, the decomposition potentials of the impurities ranging from approximately 0.5 to 2.0 volts.

In the recovery of uranium by precipitation, or by electrolysis at more than 2.4 V., thorium and zirconium should prove the most difficult impurities to separate. Experimental work later showed that scandium was also a troublesome impurity to separate.

3. REFERENCES.

Delimarskii, Yu.K. (1955). "The Influence of Anions on the Electrode potential of metals in Molten Salts".

Ukrain. Khim. Zhur. (1955) 21 (4) p.449-56. (A.E.R.E. Lib/Trans. 765 July, 1956).

Katz & Rabinowitch (1951). "The Chemistry of Uranium". Part I. (McGraw-Hill Book Co.)

Kortum & Bockris (1951). "Electrochemistry". Vol. 1 p.477 (Elsevier Publishing Co.)

Kubaschewski & Evans (1951). "Metallurgical Thermochemistry". (Butterworth-Springer Ltd., London).

APPENDIX 2.

CONTROL OF CHLORINATION.

1. INTRODUCTION.

Several possible methods of determining the progress and completion of chlorination were investigated, using the melt samples withdrawn as described in the text.

The means of testing the samples were :-

(a) Visual appearance of a water solution.
(b) Spectrophotometric examination of a solution.
(c) X-Ray diffraction spectrometry of the solid samples.
(d) An analytical procedure for determining oxygen associated with uranium.

The development of the analytical procedure and its application are the main contents of this appendix.

2. PRELIMINARY TESTS.

2.1 Appearance of Water Solution of the Samples

If the samples were dissolved in water, without heating, then the appearance and behaviour of the solution appeared to be a guide to the state of chlorination. The following stages were distinguished :-

1. Yellow solution containing insoluble oxide.
2. Completely soluble, yellow solution.
3. Yellow-green solution.
4. Green solution, easily hydrolysed on warming.
5. Relatively stable green solution.

2.2 Spectrophotometric examination of Sample Solutions

Spectrophotometric examination of these solutions established that the yellow colour of stages 1 and 2 was due to ferric chloride and uranyl chloride. By stage 4, no uranyl chloride remained, but the ready hydrolysis of the solution indicated the presence of uranous oxy-chloride. This salt was not distinguishable from UCl_4 spectrophotometrically. Stage 5, taken as indicating complete chlorination, was therefore only distinguishable by the doubtful characteristic of stability of the solution on being warmed.

2.3 X-Ray Diffraction Spectrometry of the Solid Samples

One series of six samples was submitted to the Mineralogical Section, for examination by the X-Ray diffraction spectrometer.

The graphs obtained were examined for possible peaks by which the final disappearance of oxysalts could be judged.

Although the build-up and the reduction of uranyl chloride (similar to that indicated in stages 1, 2 and 3 in para. 2.1) could clearly be followed on the X-ray diffractographs, there were no definite peaks attributable to uranous oxy-chloride. This method was therefore of no value.

3. ANALYTICAL DETERMINATION OF OXYGEN ASSOCIATED WITH URANIUM.

3.1 Theory

An analytical approach was worked out in theory.

Possible compounds of uranium mentioned by Katz and Rabinowitch (1951), which could be present during chlorination, ranged from UO_3 or UO_2, through $UOCl_4$, UO_2Cl_2, $UOCl_2$, UCl_3, UCl_4 to volatile UCl_5 and UCl_6. It was obviously not possible to determine all of these compounds individually, but an over-all distribution of oxygen and chlorine could be determined on each sample as follows :-

(a) Total uranium determination, giving "x" g. atoms of U per unit of melt, or 6x g. equivalents of U, if all the U were hexavalent.

(b) Titration of the solution with dichromate, giving indirectly the average valence state of the uranium. "y" g. equivalents of dichromate per unit of melt was a measure of the difference between the actual valence state of the uranium and the hexavalent state assumed in (a).

(c) Titration of the water solution of the sample with standard NaOH to the completion of the precipitation of the uranium. From the equations below it can be seen that the consumption of NaOH is a measure of the chlorine associated with the uranium :-

$$UOCl_4 + 4\,NaOH \longrightarrow 4\,NaCl + UO_3.H_2O + H_2O$$
$$UO_2Cl_2 + 2\,NaOH \longrightarrow 2\,NaCl + UO_3.H_2O$$
$$UOCl_2 + 2\,NaOH \longrightarrow 2\,NaCl + UO_2.H_2O$$
$$UCl_4 + 4\,NaOH \longrightarrow 4\,NaCl + UO_2.H_2O + H_2O$$
$$2\,UCl_5 + 10\,NaOH \longrightarrow 10\,NaCl + UO_2.H_2O + UO_3.H_2O + 3\,H_2O$$

Providing some suitable means of determining the end of the precipitation was available, then "z" g. equivalents of NaOH per unit of melt would give the number of g. equivalents of chlorine associated with the uranium.

With x g. atoms of U, a maximum of 6x g. equivalents of chlorine and/or oxygen can be associated. Since y g. equivalents of dichromate are taken up by this amount of uranium, only 6x - y g. equivalents are available for oxygen and chlorine. The amount of oxygen (in g. equivalents) is thus represented by 6x - y - z.

An oxygen/uranium ratio may then be calculated and expressed as percentage chlorination, assuming a 3:1 atomic ratio (UO_3) as zero chlorination, and a nil ratio (UCl_4 or UCl_5 with no oxysalts) as 100 percent chlorination.

Iron, and other impurities, which will precipitate with NaOH must be determined and allowed for at their normal oxidised valence states.

3.2 Sodium Hydroxide Titration

Synthetic solutions of uranium chloride were made from pure UO_3.

<u>Solution A</u> <u>Uranyl chloride (UO_2Cl_2)</u>, containing

21.2 g/l. U)
10.6 g/l. Cl) determined by analysis.

Approximately 0.1 N free acid.

<u>Solution B</u> <u>Uranous chloride (UCl_4)</u>,

Produced by electrolytic reduction of a solution of the same composition as A above. The solution was electrolysed for a prolonged period in the cathode compartment of a cation-permeable membrane cell. The reduced solution was aerated for two hours to ensure that any UCl_3 was re-oxidised to UCl_4.

19.9 g/l. U)
10.6 g/l. Cl) determined by analysis.

Free acidity practically nil.

These solutions were titrated with standard NaOH solution both conductometrically and by following the pH change. Best agreement between theory and practice was obtained by titration of uranyl chloride using pH measurement. The end-point inflection at pH 6 coincided with the theoretical titration figure.

It was decided to oxidise all solutions with hydrogen peroxide before titrating. Most of the uranium was precipitated as uranium peroxide, liberating free acid which was then titrated. Methyl red indicator could be used in place of a pH meter, pH 6 being the point of no further change of colour. It was shown that the addition of excess peroxide did not affect the NaOH consumption. In order to obtain a better end-point in the presence of ferric hydroxide precipitate, the methyl red indicator was screened with methylene blue.

3.3 Procedure with Samples

During chlorination tests, samples of melt were withdrawn at suitable intervals, weighed and dissolved in measured volumes of pure water, so that suitable aliquots of the solution could be taken for assay.

When crude oxide was being chlorinated, assays for uranium, iron and sometimes titanium were made. All other impurities which were precipitable with NaOH were estimated from the known ratios of impurities to uranium in the crude oxide. Aliquots of the solution were titrated with 0.1 N dichromate and with 0.1 N NaOH.

The following formula was then applied :-

Oxygen (g. equivalents) = (6 x U g. atoms) + (3 x Fe g. atoms) + other impurities (g. equivalents) - NaOH (g. equivalents) - $K_2Cr_2O_7$ (g. equivalents).

From this figure, the oxygen/uranium ratio and hence percentage chlorination was calculated.

From the dichromate titration, the average valence state of the uranium could also be calculated. In a fully chlorinated melt, this meant that the proportion of uranium present as UCl_5 was known, and the correct quantity of magnesium required for reduction could be calculated.

3.4 Probable limits of error

The maximum possible spread of error in the determination of percentage chlorination was of the order of ± 5 per cent when near 100 percent chlorinated, but from the tests carried out so far the normal spread of error in any one test was no more than ± 1 percent.

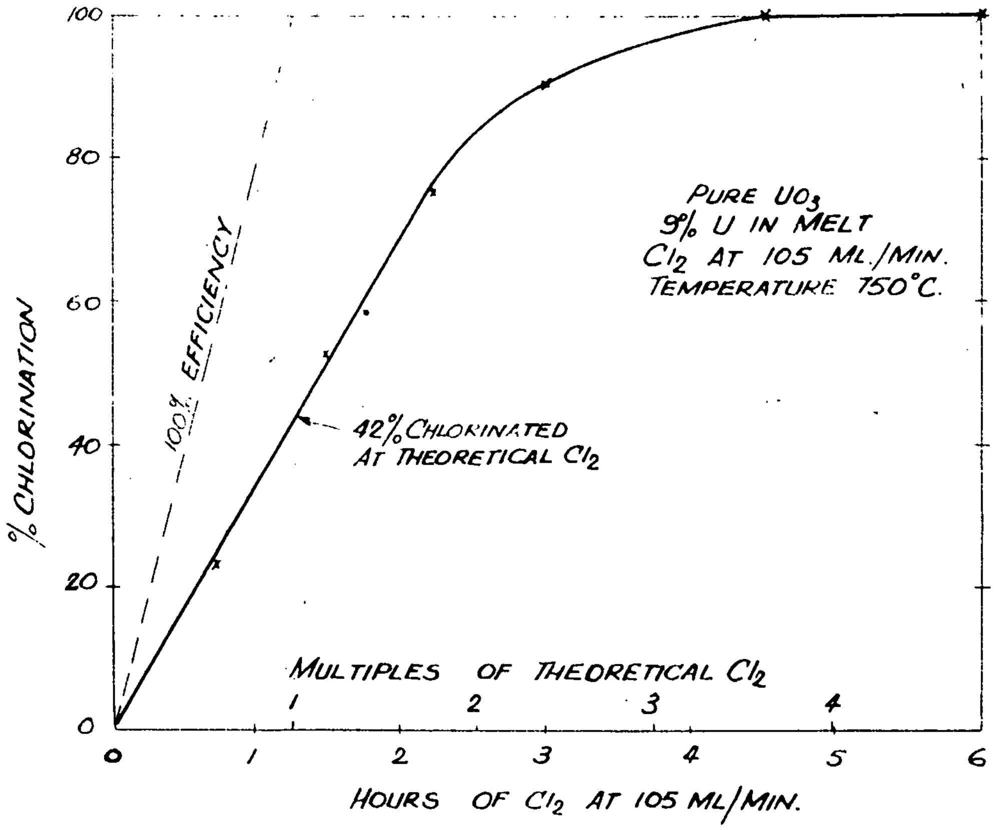
4. TEST CHLORINATION OF PURE UO_3.

A chlorination of pure UO_3 was carried out to provide a series of samples to test the above method of determining the degree of chlorination. Pure UO_3 was used as feed in order to simplify the analytical procedure.

Temperature was maintained at 750°C.

The results of the analyses of progress samples from this test are summarised in Table 10. The rate of chlorination is shown graphically in Figure 12.

FIGURE. 12.



CHLORINATION OF PURE OXIDE

TABLE 10.

CHLORINATION OF PURE UO_3.

Sample No.	1	2	3	4	5	6
Time - hours	0.75	1.5	2.25	3.0	4.5	6.0
Fraction of theoretical Cl_2 added.	0.6	1.2	1.8	2.4	3.6	4.8
Appearance of solution of Sample	yellow (some insol.)	yellow/ green	green	green	light green	light green
U content - mg. atoms per 1 g. melt	.375	.375	.375	.370	.372	.382
$K_2Cr_2O_7$ titration mg. equivs. per 1 g. melt	.044	.216	.433	.638	.719	.711
NaOH titration mg. equivs. per 1 g. melt	.485	.95	1.25	1.41	1.52	1.57
Calculated oxygen mg. equivs. per 1 g. melt	1.72	1.08	.567	.172	-.007	.011
O : U ratio (atomic)	2.3	1.44	0.75	0.23	-0.01	.014
Percentage chlorination of UO_3.	23%	52%	75%	92%	100%	99.5%

5. DISCUSSION.

The test chlorination illustrated in Fig. 12 showed that the analytical method of determining oxygen in the melt would provide a reasonable form of control of the chlorination reaction. The relatively small scatter of points about a smooth curve indicated only a small haphazard error in the determinations, and the general validity of the method was confirmed by the fact that the curve flattened out at 100% chlorination.

It was noted in Table 10 that at the stage where No. 3 sample was completely soluble, giving a green solution, the uranium was only 75% chlorinated. This implied that enough oxygen was present for 25% of the uranium to exist as UO_3, or 75% of the uranium to exist as $UOCl_2$. As the uranium was completely soluble, giving a green solution, the latter was obviously the case. After the theoretical quantity of chlorine had been passed, only 42% chlorination had been achieved and over 3 times the theoretical amount of chlorine was necessary to ensure 100% chlorination. The danger of relying on the visual appearance of the sample solutions as a guide to completion of chlorination was emphasised by comparing visual appearances with the analytical determinations.

The analytical work on each sample, including weighing the cooled sample and dissolving in a measured volume of water, could be completed in little more than one hour, provided the necessary equipment and reagents were prepared and ready for use. The services of two assistants would be required to enable rapid uranium and iron assays to be carried out without delay.

The use of this procedure as a process control was considered to be quite feasible, the delay of one hour being well worth-while in order to obtain an accurate estimate of the state of the melt. However, in most of the laboratory tests, it was more convenient to carry out assays and calculations, and to draw the graph showing the rate of chlorination, after the experimental run was completed.

6. REFERENCE.

Katz and Rabinowitch (1951). "The Chemistry of Uranium". Part I. (McGraw-Hill Book Co.)