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DEPARTMENT OF MINES

South Australia

RESEARCH AND DEVELOPMENT BRANCH

REPORT OF OVERSEAS VISIT

4th September, 1956 to 19th November,
1956.

by

J. D. HAYTON.
CHIEF RESEARCH CHEMIST.

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SUMMARY.

This report covers the period from 4th September, 1956 to 19th November, 1956. During this time the author visited Atomic Energy and other establishments in the United Kingdom and made a brief visit to several ceramics firms in Germany.

For convenience, the report is divided into sections under the following main headings :-

Section 1	..	Uranium Metal - The Gibson Process.
Section 2	..	A.E.R.E., Harwell.
Section 3	..	Other Atomic Energy establishments.
Section 4	..	C.R.L., Teddington.
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SECTION 1 ..

Uranium Metal - The Gibson Process.

The main purpose of the visit was to discuss with Mr. A.R. Gibson of A.E.R.E., Harwell, the process suggested by him for production of uranium metal. Experimental work in Adelaide on this process had reached a stage where additional experience and advice were considered to be desirable. It was hoped to obtain information regarding improvements in the process and to discuss the properties of materials for use in containing the molten salts used in the process.

Some time was spent at Harwell with Mr. Gibson but no experimental work was carried out. It was clear that there had been very little progress made since the visit to Harwell in 1954 of Messrs. Canning & Dixon of this Department. There were no experimental data available to enable an evaluation to be made of steps in the process and it was obvious that some of the work carried out in our own laboratories was at least as advanced as that at Harwell.

Subsequently some tests were carried out in an associated laboratory at Gloucester. The tests were on a slightly larger scale than those previously carried out at

Harwell and were intended to investigate the recovery of uranium metal from the Port Pirie Chemical concentrate. The author was present during most of the tests and was able to form some opinions of the likely future of the process.

It was apparent that the initial stage of the process in which the oxide is converted to chlorides could be carried out successfully. In this operation, the progress of the chlorination was followed successfully by use of the analytical procedure developed in the Laboratories at Parkside. The tests did not proceed beyond the next stage which was aimed at removal of the iron and other impurities by electrolysis.

It was concluded from the results of these tests and from discussions held with various officers that the process would not be suitable for use with impure starting material, viz., Port Pirie chemical concentrate. Some work has been carried out all ready in the Parkside Laboratories with the object of producing the uranium oxide in a pure form suitable for subsequent recovery of the uranium metals. It has been shown however, that the molten salts containing uranium chlorides attack ceramic materials resulting in reoxidation of the uranium and contamination of the final product. It is considered that the only material suitable for use in containing the melts is graphite and care must be taken in using this material to avoid formation of uranium carbide.

SECTION 2 ..

A.E.R.E., Harwell.

While at Harwell visits were made to other sections which were considered likely to be of interest.

The chemistry division had been concerned mainly with solvent extraction studies for the recovery of various metals from solution. Much of the experimental work was carried out in mixer-settler units made of pyrex glass. The units were designed to operate continuously at small flow rates.

Interest in the Analytical Division was mainly in improved techniques for radiochemical analysis. A "square wave" Polarograph had been developed and was used for determining elements in complex mixtures. Ion exchange and chromatographic techniques were used in separating fission products and considerable use was made of recently developed electronic equipment for determination of small amounts of elements in solution.

In the Chemical Engineering Division a programme of work on development of solvent extraction equipment was in its final stages. Most of the work was concerned with the construction of pulse type columns which had been found satisfactory for large scale operation. The ore dressing section was notable for the standard of cleanliness which was maintained rigidly. The equipment was designed to reduce dust contamination to a minimum and the whole layout appeared to be most effective.

Graphite technology was discussed with Mr. J.M. Hutcheon who was in charge of a programme for the production of graphite billets for experimental use. The billets were extruded from high pressure dies and fired in suitable furnaces. Some of these billets would probably be made available on request.

A group working under Dr. E. Glueckauf was concerned with the recovery of radioactive constituents from fission product waste liquors. Ion exchange techniques had been used but the synthetic resins could not be used at high temperatures and pressures. Alternative materials in the form of oxy salts of zirconium and thorium were being investigated and some success had been achieved.

Various types of reactors were inspected briefly and some of the proposed investigations were discussed. In an interview with Dr. Dalton of the A.A.E.C. ~~it~~ was stated that materials of construction and containment would continue to be a major study both in U.K. and Australia. It was also indicated that the metals zirconium, lithium and beryllium were likely to be of major importance in future atomic energy programmes.

SECTION 3 ..

Other Atomic energy establishments.

A visit was made to the establishment at Springfields where uranium metal is produced from crude oxide such as the Port Pirie material. Various aspects of chemical research were discussed with officers of the Research and Development Section and the physical and Metallurgical Laboratories were visited. It was apparent from the considerable amount of work in progress in the latter laboratories that the problems associated with uranium fuel processing and handling were extremely complex.

At Windscale some of the Reactor Research was explained, particularly the use of metallic sodium as a heat exchange medium. The chemical and physical laboratories were visited and discussions were held with members of the staff.

SECTION 4 ..

Chemical Research Laboratories, Teddington.

The laboratories are a part of the National Physical Laboratories at Teddington and a large part of the work is concerned with aspects of Atomic Energy.

The inorganic Section were interested in methods of separation of lanthanons using ion exchange techniques and were also concerned with the recovery and purification of rare metals. The rare metal selenium was mentioned as likely to be in demand in the future and it was suggested that sources should be sought in S.A.

The high polymers group were investigating the preparation and properties of synthetic ion exchange resins. Fundamental studies were in progress in an attempt to determine the nature of the complex mechanisms involved. The preparation and application of ion exchange membranes was also under investigation.

In the Radiochemical Laboratories the work included investigation of the use of ion exchange resins for recovery of gold from cyanide solutions and for recovery of uranium from leach liquors. Current studies included the use of conventional column methods and a "Resin in pulp" procedure for the treatment of leach liquors from the "Mary Kathleen" ore. The use of solvent extraction techniques for recovery of uranium from liquors was also being investigated. The methods used were similar to those applied in Canada and the United States. The analytical section of this Group was actively engaged in developing and improving methods for the estimation of the constituents of radioactive ores.

SECTION 5 ..

Other establishments visited.

At the Royal School of Mines which is part of the Imperial College, the main interest was in the Mineral Dressing Laboratories. The equipment and techniques used were mainly conventional and only a limited amount of research work was in progress. An interesting application of pressure leaching techniques was the recovery of zirconium salts from zircon sands. Details of the process were not disclosed but it appeared to be fairly simple, involving the use of sodium hydroxide under controlled conditions. It was claimed that the process could be applied also to the recovery of tantalum and niobium from ores.

The Fulmer Research Institute at Stoke Poges carried out work on research projects sponsored by organisations concerned with metals production and fabrication. The equipment was mainly of a physical or physical chemical nature and included X-ray diffraction and electron microscope units. A considerable amount of work had been done over a period of years on the development of a process for recovery of certain metals from their alloys with irons. Metals such as aluminium and titanium had been recovered by a process involving initially, reaction of the higher chlorides of the respective metals with the corresponding ferro alloy. The metals were subsequently recovered by decomposition of the mixed gaseous chlorides under controlled conditions.

It was ascertained that the Institute was prepared to accept Research Staff from other organisations and had in fact accommodated several Commonwealth Officers in recent years.

Other organisations which were visited included The Thermal Syndicate Ltd. at Wallsend; The British non-Ferrous Metals Research Association; the Chalk Lime and Allied Industries Research Association; The Permutit Co. Ltd., and the Morgan Crucible Co., all of which were in or near London.

SECTION 6 ..

Visits outside the U.K.

Brief visits were made to the Degussa Co. ceramic premises in Frankfurt and to the Haldenwange porcelain manufacturers in Berlin. The object of the visits was to discuss requirements for ceramic materials suitable for use in molten salt electrolysis.

The Degussa organisation manufactured only oxide materials such as alumina, zirconia, thoria etc. and the materials were not considered to be satisfactory for the purpose intended.

The sales and laboratory personnel of Haldenwange were most courteous and helpful in discussing the problems. It was concluded that the ceramic ware known as "pythagoras" would be the most suitable material to use for containing the molten salts.

SECTION 1 .. URANIUM METAL - THE GIBSON PROCESS.

1. INTRODUCTION.

The Gibson process for the production of uranium metal from impure oxide was first referred to in 1954 during the visit to Harwell of Messrs. P. Dixon and R. Canning. The process as described at that time depended on the reaction of crude oxide with chemical agents in a melt of sodium and potassium chlorides contained in a suitable refractory vessel. The oxide was reduced by the addition of either sodium sulphide or barium sulphide with simultaneous injection of chlorine gas to convert the oxides to chlorides. The purification of the chloride melt depended on precipitation of impurities such as iron, by addition of a suitable amount of magnesium metal. At this stage the melt was decanted from the precipitated impurities and the Uranium metal was similarly precipitated by Mg in another vessel. The Uranium metal was subsequently recovered by electrolytic transfer to a cathode which was generally made of molybdenum.

It was later proposed by Gibson that certain modifications be introduced to the process originally described. In the conversion stage it was found more convenient to use a block of carbon as the reducing agent. The block served also as a distributor for gaseous chlorine. By this means the addition of chemical reducing agents was eliminated. The converted melt which contained Uranium as UCl_4 was treated further by the injection of H_2 gas to reduce the UCl_4 to UCl_3. At this stage, the Mg precipitation technique could be used as before. It was further proposed however that an electrolytic procedure should be adopted. The iron and other impurities having lower decomposition potentials than that of uranium should be deposited first, leaving uranium to be recovered in a later stage. Considerable difficulties were experienced in this procedure both at Harwell and in the Research & Development Laboratories in Adelaide and it is doubtful whether a pure product could be obtained by this means.

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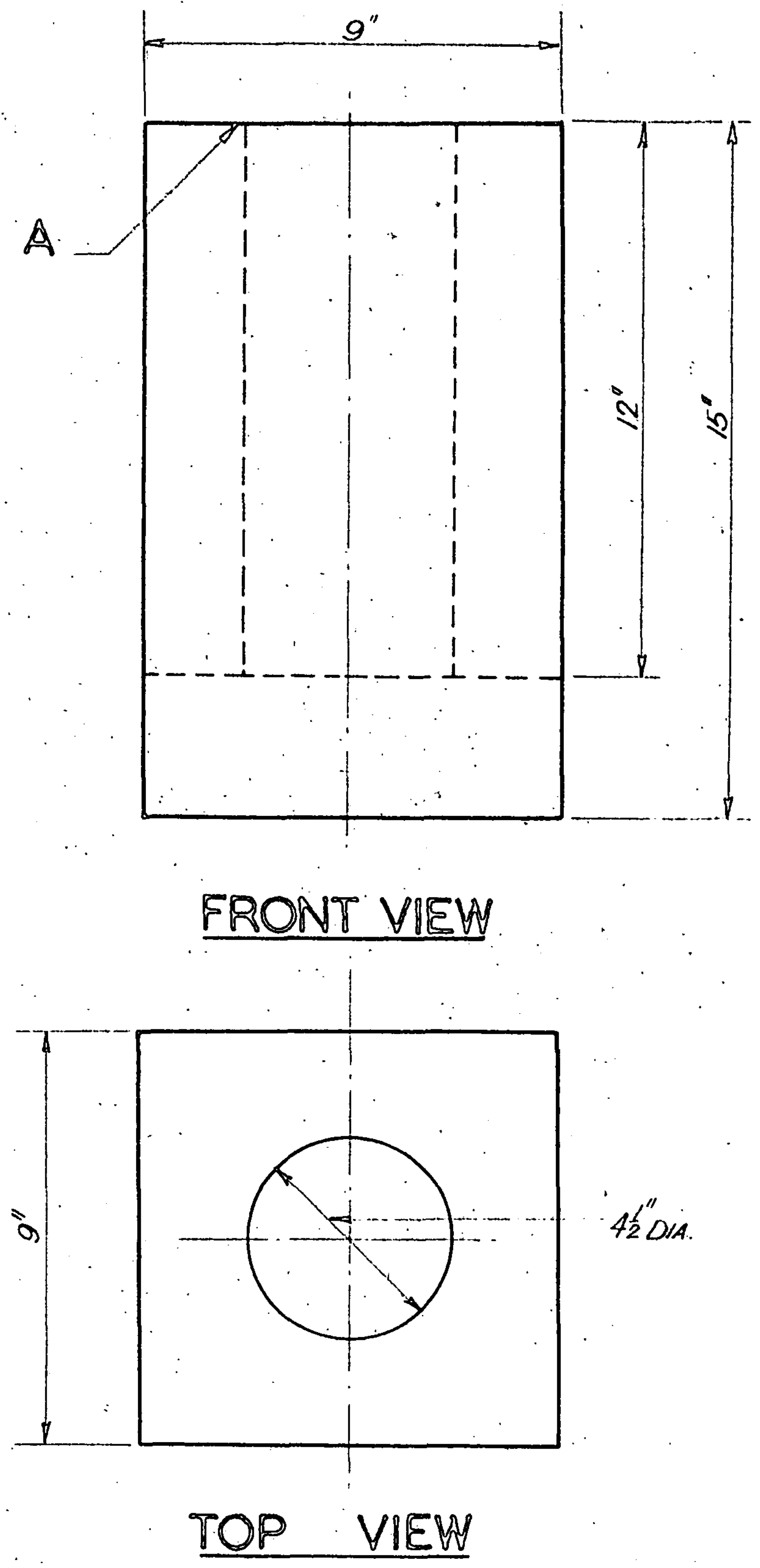


FIG.-1.

A	Silica Tube Recessed ¼"
	NOTES
3	Outer Walls of "Syndanyo" Asbestos Board
2	3" Base of Firebrick.
1	17 Gauge Nichrome Wire Winding 0.633 Ω Per Yard. Total Resistance 47 Ω (Approx 1KW Capacity)
	MATERIALS

2. LABORATORY TESTS.

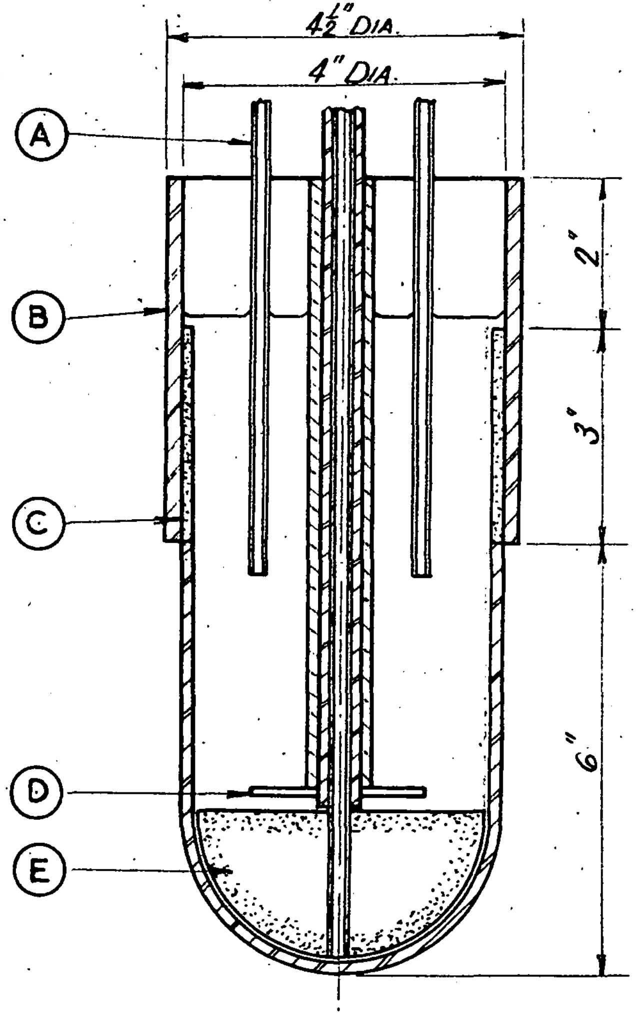
2.1 Procedure

The laboratory set up was much the same as when P. Dixon and R. Canning were at Harwell. Conversions were carried out in a 3 inch diameter silica crucible contained in a small wire wound silica furnace (Fig. 1). Both argon and hydrogen gas used in the experiments were deoxygenated before use. The argon was passed through a small tube furnace packed with Mg metal turnings at a temperature of 400°C, while the hydrogen was passed through a small catalytic attachment."/ Argon and hydrogen lines were connected to a mercury blow off bottle in case of blockage of tubes during a run. The source of current for electrolysis was a rectifier with primary voltage controlled by means of a "Variac" transformer. This equipment provided current up to 50 amps. The method for conversion of the melt was much the same as now used at Parkside. Generally the procedure was as follows - The C distributor was just covered with molten NaCl-KCl eutectic; this quantity was about 350 g. The introduction of chlorine was commenced and the impure oxide was added slowly until about 400 g. had been added. The melt contained at this stage about 40-50% uranium and could be treated directly or else used as a master melt for further work. It was agreed that there was likelihood of some hydrolysis and oxidation of melts during pouring but it was considered that this would not be serious on a large scale and that any remaining oxysalts would be removed as UO_2 during H_2 injection and subsequently deposited electrolytically along with Fe etc.

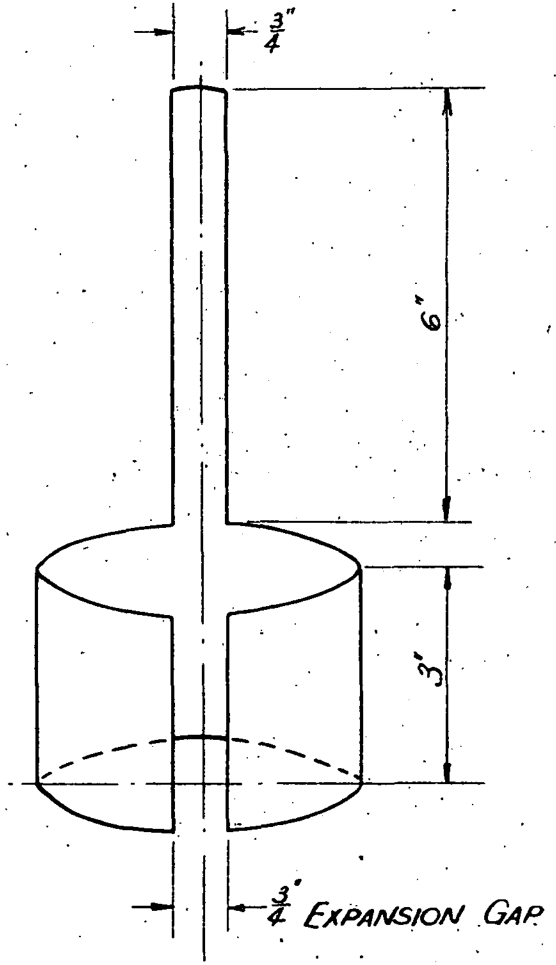
Hydrogen was introduced during the latter part of the conversion and it was stated that the end product obtained was red-brown in colour, presumably due to the presence of UCl_3. Although it was stated that electrolytic removal of Fe etc., was not difficult and had been carried out successfully many times, no experimental evidence was advanced to prove this.

"/ Catalytic purifier for electrolytic hydrogen.
DEOXO, Baker Pty. Ltd., High Holborn, London. W.1.

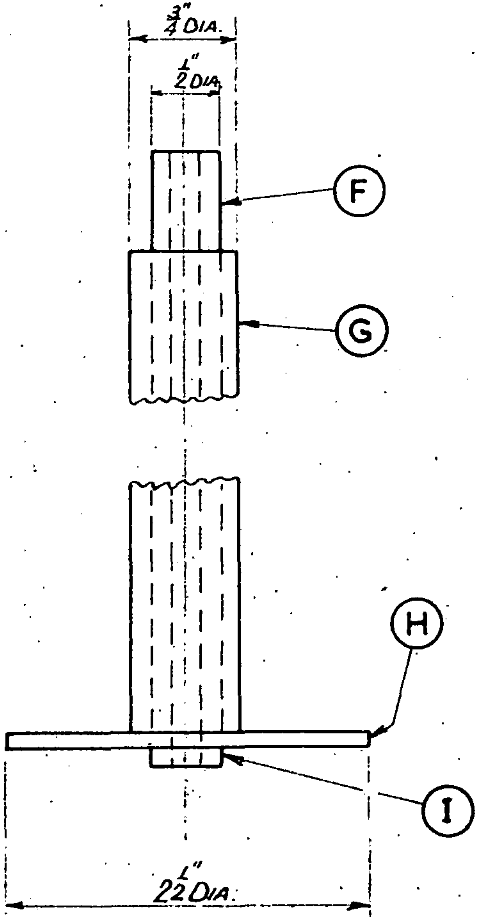
R.S.241.



SECTION OF FURNACE
FIG.-2A.



ANODE
FIG.-2B.



CATHODE
FIG.-2C.

A	HYDROGEN INLET
B	MELT LEVEL
C	ANODE OF GRAPHITE
D	CATHODE
E	CARBON DISTRIBUTOR
F	Ni Ne TUBE OVER DISTRIBUTOR SHAFT
G	ALUNDUM
H	MOLYBDENUM DISC.
I	WASHER OR WELD.

According to the decomposition potentials of impurities in the Port Pirie chemical concentrate, the most likely contaminants in the uranium metal product would be Sc and Th. Ca, La, Y, Mg have decomposition potentials higher than 2.3V (U, Sc, Th) whilst those of Al, Mn, Ti, V, Cr, Fe, Pb, Cu, Ni are below 1.96 V in diminishing order. A Ni-Fe alloy cathode was used in the electrolysis stage for iron removal and the cell was operated at 1.4 - 1.5 Volts. The constituents were maintained in a reduced condition by passing hydrogen into the melt. Although iron and other impurities should have been precipitated on the cathode at this stage, the melt was decanted before uranium recovery was attempted. Generally the procedure was to pour the melt into large nickel crucibles, cool, break up into pieces and store in a desiccator. The lumps were remelted for uranium electrolysis. It was proposed to attempt the complete process in one crucible by using equipment of suitable design as shown (Fig. 2A).

It was proposed to carry out the conversion as usual using chlorine and hydrogen injection. The iron and other impurities would be removed electrolytically without withdrawal of the carbon distributor. The cathodes were made so that the hollow Ni-Fe alloy tube fitted over the shaft of the distributor (Fig. 2C).

The Ni-Fe tube was insulated from the melt by means of a closely fitting alundum or mullite tube which did not need to be tightly sealed. The cathodes were flat circular discs generally made of molybdenum welded on to the Ni-Fe tube. Gibson had used saucer shaped ceramic discs with the metal cathode resting in the flat centre position, but considered that they would not be feasible for large scale work. A ring anode (Fig. 2B) would be placed in the upper stepped portion of the silica crucible in an attempt to direct the current flow so that deposition of metal would be on the upper surface of the cathodes rather than at the edges. It was intended that the cathode containing precipitated Fe and other impurities should be removed and replaced by one of similar design having a molybdenum disc in place of the Ni-Fe alloy material. This would then be used for recovery of uranium metal by electrolysis.

At the end of the uranium electrolysis the cathode would be withdrawn above the melt to cool and to allow the melt to solidify, then transferred rapidly to a cooling vessel filled with argon gas. An atmosphere of argon would be maintained above the melt throughout the preceding processes. These steps had been carried out in the laboratory at Harwell but with a decantation stage in between.

The single cell system would be dependent upon availability of suitable crucibles of the design illustrated. It was proposed to use a crucible of this design about 5 inches diameter in the upper portion and about 4½ inches diameter in the lower portion. A crucible of this design was actually made in the laboratory at Harwell during the author's visit, but the dimensions of the sections were 3½" diameter and 3" diameter respectively. The two sections of the crucible were welded together by means of an oxygen-hydrogen flame using silica rod as a welding agent. It was reported subsequently by Gibson that the crucible was used satisfactorily for a number of experiments before a crack developed in the welded portion. The crucible was not actually used for the procedure envisaged so no data are available concerning its effectiveness.

Gibson also considered altering the design of the carbon diffuser block, so that instead of the vanes as now used, there would be a series of vertical holes drilled to allow escape of chlorine. This could result in a greater area of carbon being available for the reaction.

There were no control methods used in laboratory tests carried out at Harwell. The end of chlorination was judged by the appearance of the melt which was reddish-brown, providing hydrogen was introduced. There were no attempts made to follow the progress of the chlorination by any chemical means such as employed in our own laboratory (Appendix I).

Current densities for removal of uranium were in the range 40-60 amps/sq. Dec or 360-500 amps/sq.ft. approx. This applied only at the commencement of the electrolysis since the cathode area would increase with deposition of metal. The product obtained was said to be dendritic and non-pyrophoric. Chemical tests carried out by the author on some of the "Uranium metal" samples showed that they contained considerable amounts of uranium oxide.

In typical electrolyses carried out in the laboratory at Harwell, the following conditions were used.

The lower end of the anode was about 3 inches above the flat cathode disc. (The stepped silica pot was intended to obviate the necessity to remove the anode assembly which formerly had been placed in the melt in a straight sided pot). Electrolysis current was 8 amps at 2.75 - 3.3 volts. There was some tendency for the product to build up at the edges of cathode, but it was claimed that under these conditions very little uranium was lost by falling to the bottom of the crucible. Any such loss would be recouped in the next run carried out in the same pot without first emptying, the carbon distributor remaining in place throughout. During the period of the author's visit to Harwell no successful runs were carried out for the removal of impurities from the melt or for the recovery of uranium metal.

2.2 Reports of Laboratory Tests

Some details of laboratory tests were given by Gibson at a discussion held later at The Chemical Research Laboratories, Teddington. The Port Pirie chemical concentrate which was representative of the material used in laboratory work at Parkside was used in these tests.

300 grams concentrate were used in each test in a eutectic mixture of 300 g. NaCl-KCl.

Run (1) :

Chlorine was passed for three hours during the conversion stage and hydrogen was introduced during the last hour to reduce UCl_4 to UCl_3. The melt was diluted with NaCl-KCl to approx. 1600 g. total weight, (11-12% U) and electrolytic removal of Fe was attempted. The melt was electrolysed at 2.5 - 3.0 volts and the total current passed was equal to 30 ampere hours. The cathode product was small and consisted of a mixture of metallic iron and UO_2. Very little iron was removed at this stage. The uranium in the melt was then precipitated by introducing air which presumably produced UO_2. In the absence of uranium in the melt it was then possible to remove electrolytically all the iron remaining. This was accomplished at 3.0 volts with a total current passed equal to 20 ampere hours. The test was not continued beyond this stage but it was intended that the precipitated uranium should be reconverted to UCl_4 by re-introduction of the carbon block and passage of chlorine as in the first step. The uranium metal could then be recovered electrolytically.

Run (2) :

The conversion of crude oxide followed the procedure in Run (1) but no hydrogen was introduced during the last hour. The titre of NaOH solution per gram of melt (dissolved in distilled water) was the same as that obtained in Run (1), viz. 30 ml/g. When hydrogen was introduced, the titre dropped to 20 ml/g. indicating loss of uranium probably as UO_2. This may occur as a result of reduction of $UOCl_2$. -

$$2\ UOCl_2 + \tfrac{1}{2}\ H_2 \longrightarrow UO_2 + HCl + UCl_3$$

It was reported that it was not then possible to precipitate all of the uranium as UO_2 by introduction of air as in Run (1). Approximately 3% uranium remained in the melt equal to 25% of the total.

The results of these tests indicate the need for much more detailed laboratory investigation before a true evaluation can be made of the process.

2.3 Alternative Processes

During the visit to Harwell several modified procedures were referred to by Gibson and one of them was in course of trial.

(1) It was suggested that pure uranium oxide (UO_2) could be reduced to the metal by means of metallic calcium produced electrolytically at the cathode in a fused salt bath. The calcium metal would presumably reduce the UO_2 to uranium metal forming calcium oxide which would dissolve in the melt, a eutectic of $CaCl_2 - KC_1$. This procedure had not been attempted but may be workable. A possible variation of this procedure would be the introduction of a small carbon block diffuser into the melt. With the addition of chlorine, the calcium oxide in the melt could then be reconverted to $CaCl_2$ by the Gibson conversion process.

(2) The conversion of oxide to chloride by anodic chlorine in a porous compartment using graphite as the anode. Gibson had used this technique for conversion of Tho_2 to

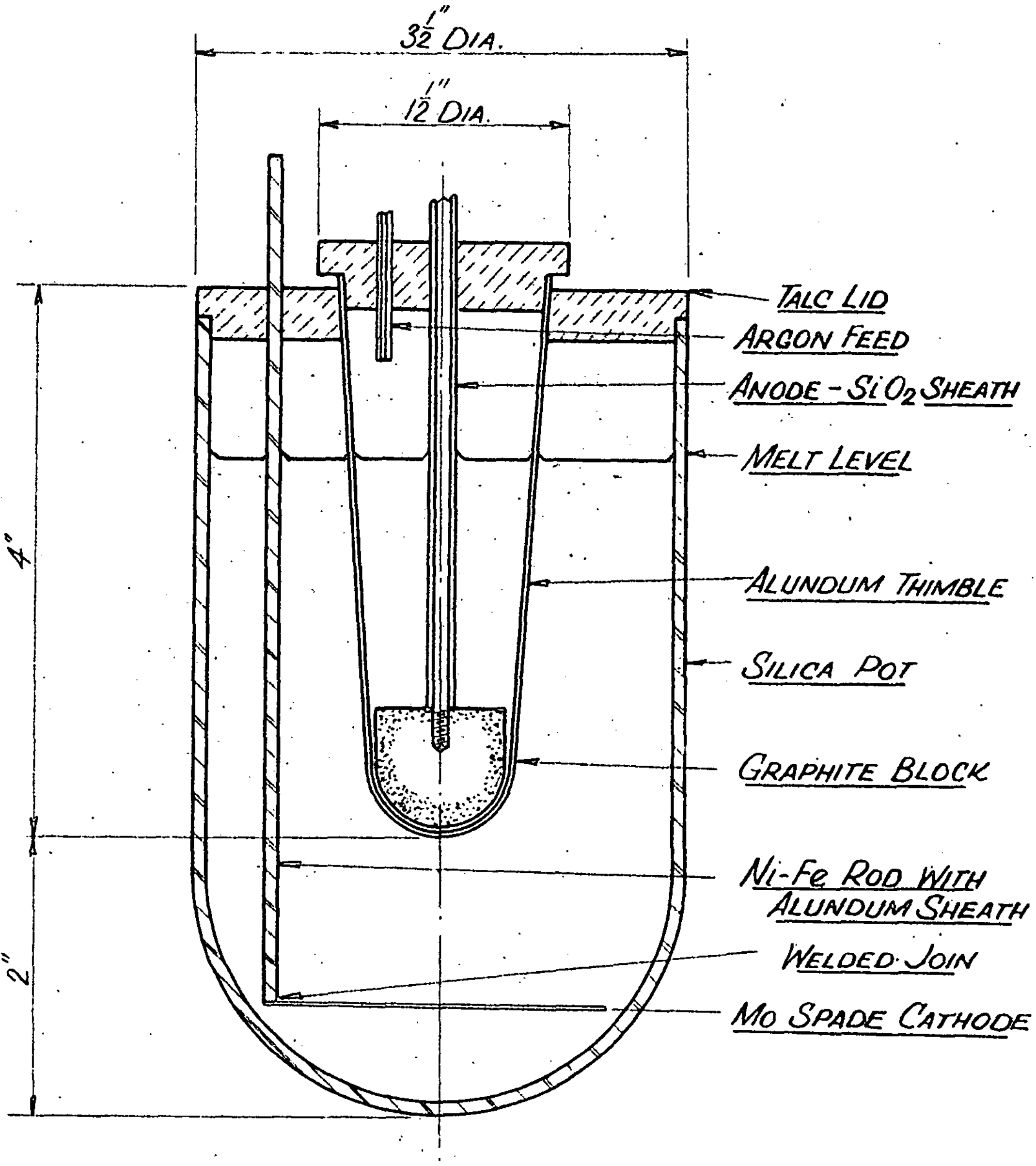

3½" DIA.
1½" DIA.
4"
2"
TALC LID
ARGON FEED
ANODE - SiO_2 SHEATH
MELT LEVEL
ALUNDUM THIMBLE
SILICA POT
GRAPHITE BLOCK
Ni-Fe ROD WITH ALUNDUM SHEATH
WELDED JOIN
Mo SPADE CATHODE

FIGURE - 3.

$ThCl_4$ and was attempting to make it continuous. It was found necessary to apply slight pressure to the anode compartment periodically to assist the melt to diffuse through the walls of the vessel into the catholyte. Argon gas was used for this purpose and on releasing the pressure, the melt flowed back into the compartment.

The initial attempt to convert UO_2 by this means was made in the apparatus (Fig. 3).

The anode compartment consisted of a porous alundum thimble about 1 inch diameter at the top, tapering to ¾ inch at the bottom and 3 inches in length. This was fitted into a talc lid which covered the main silica crucible containing the cathode and catholyte melt. A small talc lid was made to fit the top of the alundum crucible, with holes to allow the entry of the anode connection and gas or oxide feed tubes. It was necessary to seal the lid to the alundum thimble in order to obtain sufficient pressure of argon to force the melt through the porous walls when required.

In the test carried out at Harwell, crude South Australian uranium oxide was fed into the anode compartment in batches of 10 grams. The cathode compartment contained 500 grams NaCl-KCl eutectic containing initially 8 percent uranium converted to chloride by the conventional process. The cell current during the test was about 4.5 amps at 3.5 - 3.8 volts. There was no evolution of chlorine during the first 30 minutes after addition of each 10 gram charge of oxide indicating that some conversion was taking place. When chlorine began to evolve, the contents of the anode vessel were discharged into the catholyte compartment by means of argon pressure, and the mixed melt was allowed to flow back under its own head. The addition of a fresh batch of oxide to the anolyte caused an immediate rise in cell current to a maximum of 5.2 amps while the e.m.f. dropped to 3 volts. Gibson attributed this to a depolarising effect due to formation of UO_2Cl_2. The conditions rapidly reverted to those prevailing before discharge of the anolyte.

60 grams UO_2 (or U_3O_8) were added during the run which was interrupted overnight with argon passing into the

top of the pot at reduced temperature. The anode compartment was discharged by argon pressure after conversion of each ten gram lot of oxide. The electrolytic product which adhered to the upper surface of the cathode on removal from the melt had the brown appearance similar to the products of unsuccessful runs at Parkside. There could be several reasons for this.

(1) Incomplete chlorination of original melt which formed the catholyte (8% uranium).

(2) Oxidation and/or hydrolysis during introduction of anode pot assembly.

It was in fact, observed at the time of introduction of this assembly that there were ominous spitting and crackling sounds while water vapour condensed at the top of the silica anode sheath.

(3) Incomplete chlorination and reduction of oxide in the anode pot after each fresh addition of oxide. The length of each chlorination stage was judged by (a) approximate number of amp-minutes required for conversion of 10 grams UO_2 at current passing; (b) appearance of free chlorine above the anode compartment. The time allowed may have been insufficient and as no control methods were used, UO_2 could appear in catholyte. The use of suitable analytical procedures would probably make this stage more controllable.

(4) Attack by the catholyte on the alundum anode vessel. It was observed after the test, that the outside surface was badly chipped, obviously due to flaking off of alundum. This may have been only mechanical and there may have been no actual chemical attack.

The reason given for carrying out the test was not so much to obtain uranium metal as to show that the change in cell current was due to oxychloride formation and hence by analogy, that oxychloride is formed during treatment of ThO_2 in this manner.

The procedure outlined above may be of value, but at present would apply only to recovery of metal from pure oxide. It may be possible to remove impurities such as Fe at each stage by variation of cell current and use of interchangeable cathodes, e.g., electrolyze at say 1.5 volts immediately after discharge of anode contents into catholyte, until all iron and other impurities were removed, then change the cathode and electrolyze at 3 – 5 volts for the remainder of the time, for recovery of uranium until the new charge in the anode pot was fully chlorinated.

3. LARGER SCALE LABORATORY EXPERIMENTS.

3.1 "Pilot Plant" at Gloucester

A considerable amount of work had been carried out on the use of the Gibson conversion process for production of pure thorium metal.

The so called Pilot Plant was run under contract by Impregnated Diamond Products Ltd. The work was under the supervision of Mr. R. Marshall and Mr. J. Chalkley and there were about six technical assistants. The Gibson electrolytic process had been applied for the production of thorium and some 25 – 30 runs had been conducted. The process as operated produced Th metal of good quality (by density determination). The raw material was high grade ThO_2 and the sole problem was the production of pure Th metal. In actual practice metallic iron was added in the form of a fine powder to act as a carrier for chlorine. Some tests were made using finely divided carbon as a reducing agent in place of the graphite block, but as far as can be ascertained it was not proposed to dispense with the metallic iron. Three batch conversions were required to provide sufficient melt for final thorium recovery by electrolysis.

3.2 Production of thorium metal

3.2.1 Conversion Procedure –

The conversion is carried out in conical bottomed silica pots so as to allow good distribution of chlorine and to allow any solid materials to move toward the bottom. The graphite distributor is made to the same shape. The pot holds about three kg. of melt and sufficient ThO_2 is added to each of three melts to provide about three kilograms of thorium altogether. The eutectic is NaCl-KCl as in the uranium metal process. Chlorine is introduced until the melt is free of solid ThO_2 and then chlorination is continued for about 1½ hours. At this stage, the distributor is removed and a conical nickel cathode dropped in which rests on the bottom of the pot. Contact is made by a nickel rod shielded by a vitreosil sheath. The anode is a spade type graphite disc suspended in the melt. Electrolysis is carried out at 9 volts and 5 - 10 amps and continued until the iron content of the melt is reduced to 5 - 10 p.p.m. There is no hydrogen introduced in this stage. After the anode and the nickel rod are removed the melt is poured by tilting the furnace. The melt is collected in heavy aluminium moulds and later crushed and stored in glass jars.

The deposited iron is scraped out of the pot and crushed for use in a recycle. Some trouble has been experienced from attack on the silica tube shielding the nickel rod cathode connection. The cause is not certain but it is thought to be due to ferric oxide or thorium metal. It is quite possible that metallic sodium or potassium may also be formed at the cathode under the conditions of electrolysis and these metals would attack the silica sheath vigorously.

3.2.2 Recovery of Metal -

The electrolysis of thorium metal is carried out in a beaker-shaped silica pot which holds about 20 kilograms of melt. A fairly elaborate procedure is used to ensure the exclusion of moisture and air from the cell during electrolysis. The melt at the commencement of the electrolysis contains 15 percent thorium. Various designs of cathode have been tried in attempts to simplify the collection of the metal, but none so far has been an outstanding success. Ceramic saucers used as underlays to flat molybdenum discs have suffered fractures due to thermal shock and chemical attack. Electrodes painted or sprayed with alumina (Al_2O_3) have tended to flake. It is likely that plain metal (Mo) electrodes will be used but this is still under discussion.

The electrolysis is normally carried out at 260 amps. and 10-20 volts. Dip samples are taken and residual thorium is determined by qualitative gravimetric methods, usually precipitation with ammonia. The thorium content of the melt is reduced to low levels, certainly less than one percent.

The metal product adhering to the cathode is leached out after suitable handling of the electrode assembly to prevent oxidation of the metal while hot. The mixed melt-metal is first leached with water in a stainless steel bath to remove from the electrode. The product is transferred to stainless steel cement mixer type vessels and agitated for some time. After standing for 1½ hours, the supernate is decanted and several decantation washes follow. The metal is then washed by agitation with 5 percent nitric acid in a similar manner. ThO_2 is recovered from the washes by precipitation with ammonia.

The metal is dried in a freeze-drier unit operating at a pressure of 200 millimicrons. Hot water is circulated in pipes under the drying trays to prevent the formation of ice in the product and consequent unsatisfactory drying. The metal product is screened into about 6 size ranges and density determinations are made on each size. The density usually decreased with decrease in particle size. This may be due to an increase in the amount of oxide remaining or to difficulties in determination of density. The density of a product considered to be of high purity is generally about 11.6 g/ml. compared with a theoretical figure of 11.72 g/ml.

An ideal size for subsequent fabrication is in the range just below 100 mesh but a considerable proportion is much coarser than this. The stripped melt is retained and used in further conversions. A colorimetric thiocyanate method is used to determine the iron remaining in the melt during the iron electrolysis stage. More complete details of plant, equipment and procedure have been obtained by F. Hartley.

3.3 Uranium Metal Tests

The equipment used at I.D.P. Gloucester for thorium production was used for attempts to recover uranium by the Gibson process.

3.3.1 Scale of Tests -

The conversion step was carried out in a silica pot with conical shaped bottom section. These pots were made each as a single unit with no welds by Thermal Syndicate Ltd.

Diameter about 4 inches. Length 12 inches.
Capacity 3 kg. melt.

The uranium concentration in melts in the conversion stage was 30 percent approximately. The graphite converter block is shaped to fit the conical section. Mullite tubes have been used to conduct the chlorine and are cemented with C60 alundum cement. In one test, a fused alumina tube was used but it corroded badly and broke half way through the run. There was evidence of considerable reaction between the alumina and the melt.

The analytical methods developed at Parkside (Appendix I) were used for control of chlorination - without actual calculation of O_2/U ratio. It was assumed that both the NaOH and $K_2Cr_2O_7$ titrations would reach a constant figure at complete chlorination providing there was no change in concentration of melt constituents. Samples were taken by dipping in a solid rod of silica and collecting melt by freezing on the surface. The rod was quickly withdrawn and the melt was flaked off into aluminium dishes. Samples of the melt were weighed separately for each titration. It was found that methyl red screened with brom cresol purple was a more satisfactory indicator than methyl red + methylene blue.

The colour change is positive, i.e., from yellow to purple-brown and the end point is easily distinguished in the presence of precipitated uranium. At equilibrium (presumed complete chlorination), titration figures are likely to show variations of ± 0.5 ml. in a titration of about 40 ml.

Results are expressed as titre/g. of melt. The officer in charge of the tests was satisfied with the results and considered the methods were most valuable in following the progress of the chlorination. The conversion stage appeared to be satisfactory but attempts to remove iron electrolytically were not successful.

3.3.2 Conversion of Crude oxides to Chlorides -

About 1.75 kg. eutectic were placed in the special silica pot and melted at 780 - 800°C. The converter block was positioned through the talc lid in which was a feed hole about $\frac{3}{4}$ inch diameter for product. At start up from fresh melt 200 g. product (ignited at 450°C.) were fed in and chlorine passed until all the solid was in solution. The addition of the main sample was then commenced to bring the amount of oxide added to 1.25 kg. The material was added by hand using a small aluminium spoon or similar utensil and the feed rate was very slow. The melt tended to froth at intervals and caution was needed in adjusting the feed rate to avoid boiling over. A dark scum formed on the surface of the melt, probably mainly carbon from the converter block. The gas evolved during the reaction, (CO or CO_2) did not seem to be the main cause of frothing. The frothing took place at intermediate times and could be reduced by addition of more solid product. The addition of 1 kg. of product usually took about three hours. By the time all the solid had been added, conversion was apparently almost complete. This was indicated by the solubility of the melt, appearance of the solution and by levelling out of the titrations of samples of the melt.

3.3.3 Electrolysis -

Hydrogen was passed into the UCl_4 melt before electrolysis and also during electrolysis. Samples of the melt were titrated with $NaOH$ and $K_2Cr_2O_7$ during this reduction but the results were not consistent. The $K_2Cr_2O_7$ titre at apparent complete reduction was low and this was undoubtedly due to oxidation of UCl_3 when the sample was exposed to air and in solution.

Electrolytic Removal of Iron :

A conical graphite cathode was used with a mild steel rod tapped in for support and conduction of current. The rod was shielded with mullite or silica tubing. The anode was of spade type with holes for cathode, tube for hydrogen, thermocouple and sample tube.

The cathode rested on the bottom of the pot and the anode was suspended so that it was just in the melt when hydrogen was passing. This arrangement allowed chlorine generated to escape without dissolving in the melt or reacting with the hydrogen which was introduced near the cathode. Results were disappointing and iron removal was poor. At low current densities, 20 amps, 6 volts, the removal rate was slow and the efficiency was very low. At higher current densities, 50 amps, 11 - 12 volts, iron was removed quantitatively, together with much of the uranium. In one test for instance, the iron content was reduced from 1.5% to 0.003% but the uranium content dropped from 30% to 17%. As far as can be ascertained, this uranium was deposited as UO_2 or at least was present as UO_2 when the cathode product was removed. There are at least four possible explanations.

(1) Incomplete conversion. This is not likely since control analytical methods were used.

(2) Oxidation during changeover of equipment, i.e. the carbon block replaced first by the hydrogen tube, then by the cathode, anode, etc.

(3) Oxygen in the hydrogen. This cannot be ruled out since in this case, no deoxygenator was used.

(4) Attack on silica and ceramics. If this is the main reason, then the future of the process does not appear bright. The colour of the hydrogen reduced melts was by no means red-brown as stated by Gibson, but rather grey to black. The red colouration formerly seen could have been due to surface oxidation.

3.3.4 Details of Repeat test -

Chlorination of a 3 kg. melt containing 30 percent uranium, which was commenced the previous day, was continued for one hour the following morning. NaOH and $K_2Cr_2O_7$ titres of samples of the melt remained constant. H_2 was passed through the melt and after three hours the electrolysing equipment was introduced. The melt was electrolysed at 35 amps, 12 volts at the start. The initial iron content of the melt determined by the phenanthroline colorimetric method (rough) was 0.87%. The iron content dropped to 0.45% in about one hour but the decrease was slow thereafter. The iron content remained at about 0.30% for three hours and at this stage the melt was decanted. The cathode product was dense and hard and consisted of a mixture of metallic iron and UO_2 but in only small amounts. It appeared that conversion of the oxide was almost complete and that little oxidation had taken place subsequently. However, the electrolysis efficiency was very low and it would appear that further investigation of conditions would be advisable.

The procedure used for the electrolysis, probably resulted in too much cell resistance and this may account for poor efficiencies. The anode and cathode were at least 6 inches apart and the voltage required was high. Better results may be achieved by decreasing the electrode distance, say by raising the cathode, rather than by lowering the anode.

Investigations of current density, electrode distances, point of addition of hydrogen, removal of chlorine and hydrochloric acid etc., would be more a laboratory project than a Pilot scale one.

Examination of the silica pot which had been used for three conversions and hydrogen reductions did not reveal any etching of the surface and it is probable that no serious contamination of the melt occurred from this source.

A very useful report is available, now declassified, which describes work carried out on electrolysis of various uranium compounds in fused salt eutectics (1).

SECTION 2 .. OTHER ACTIVITIES AT HARWELL.

1. CHEMISTRY DIVISION.

A considerable amount of work had been carried out on solvent extraction procedures for separation of metals. A particular aspect of the work was the recovery of Th using TBP-xylene mixtures. The opinion was expressed that solvent extraction procedures were most suitable for providing materials of a high degree of purity and doubts were expressed of the efficiency of electrolytic processes such as the Gibson process for Uranium Metal.

Much of the laboratory work was carried out in small glass mixer-settler units which had a modified pumping device operated by an overhead camshaft. By suitable arrangement any number of the units could be incorporated in the equipment, depending on the number of stages required in the extraction. Almost theoretical efficiency was claimed for the units. The flow rate of liquor was about 10 ml/minute on the scale used in the laboratory. The units are fully described in an A.E.R.E. report (2).

2. ANALYTICAL DIVISION.

(Head of Division - Mr. A. Smales).

The group is operating much the same as when P. Dixon and R. Canning were at Harwell. Considerable attention has been given to solvent extraction, chromatographic and ion exchange techniques for analytical methods.

2.1 Polarography

A "square wave" polarograph is in use in this section and has given good results. It use has enabled the determination of small amounts of impurities such as copper or nickel in steels, despite the presence of large quantities of iron in the ferric condition. The application of the square wave AC potential has the effect of differentiating the normal step curves, so that, instead, peaks are obtained which are most distinct. The sensitivity claimed is much greater than for normal polarography. The instrument is expensive, the cost being about £1800 sterling and it is probably more suitable as a research instrument. It is likely that cheaper models will be produced.

2.2 Ion Exchange

One application of anion exchange in analytical work has been the use of Deacidite FF for separation of bismuth, uranium and thorium in fission products. The finely divided resin, about 40 - 60 mesh, is contained in glass columns about 5 mm. diameter and 100 mm. long. The metals are passed through in HCl solution. The first pass is made in dilute HCl - not more than 3N and bismuth is adsorbed on the resin while uranium and thorium are not.

Subsequently the acidity is increased to 9N and the solution passed through another column. Under these conditions, uranium is adsorbed while thorium passes through. Uranium is determined in micro - and semi-micro amounts by use of a lead reductor. The lead used is of a high degree of purity. The reduced uranium solution is titrated with ceric sulphate solution using ferroin as indicator.

2.3 Coulometry

The development of coulometric techniques has been studied by Dr. Smythe, originally from Melbourne. The procedure can be made automatic by the use of suitable equipment but is suitable only for trace quantities. This is applied with a high degree of accuracy for instance, to the titration of chromium (VI) by cathodically generated iron (II).

2.4 Chromatography

Chromatographic paper strip techniques developed at C.R.L., Teddington, have been used for separation of radioactive constituents in solutions in very small amounts.

3. CHEMICAL ENGINEERING DIVISION.

3.1 Solvent Extraction

The work here had been confined to the study of the mechanics of extraction and to the development of equipment. The actual chemistry of solvent extraction was not considered.

The main work was done with pulse columns using perforated disc plates. Generally the size of holes in the plates was about $\frac{1}{8}$ inch and the total area about 25 percent of surface area (i.e. 25 percent "Free Space"). The group was changing to study of reactor problems, heavy water production etc.

3.2 Ore Dressing

This section contained all the usual equipment associated with ore dressing. A feature which impressed was the extreme neatness of layout which was designed to reduce dusting and contamination to the absolute minimum. A rigid standard of cleanliness was insisted upon throughout all operations and the use of this system had obviously paid dividends. The sampling of ores was controlled by one technical assistant, thus ensuring standardization of procedure and minimising confusion. Separate colour codes were used for heads, middlings, tailings and concentrates and cards of the appropriate colour were used to record details, treatment required and analytical results for each.

The technician in charge of sampling was the only person permitted to add to or remove samples from the store.

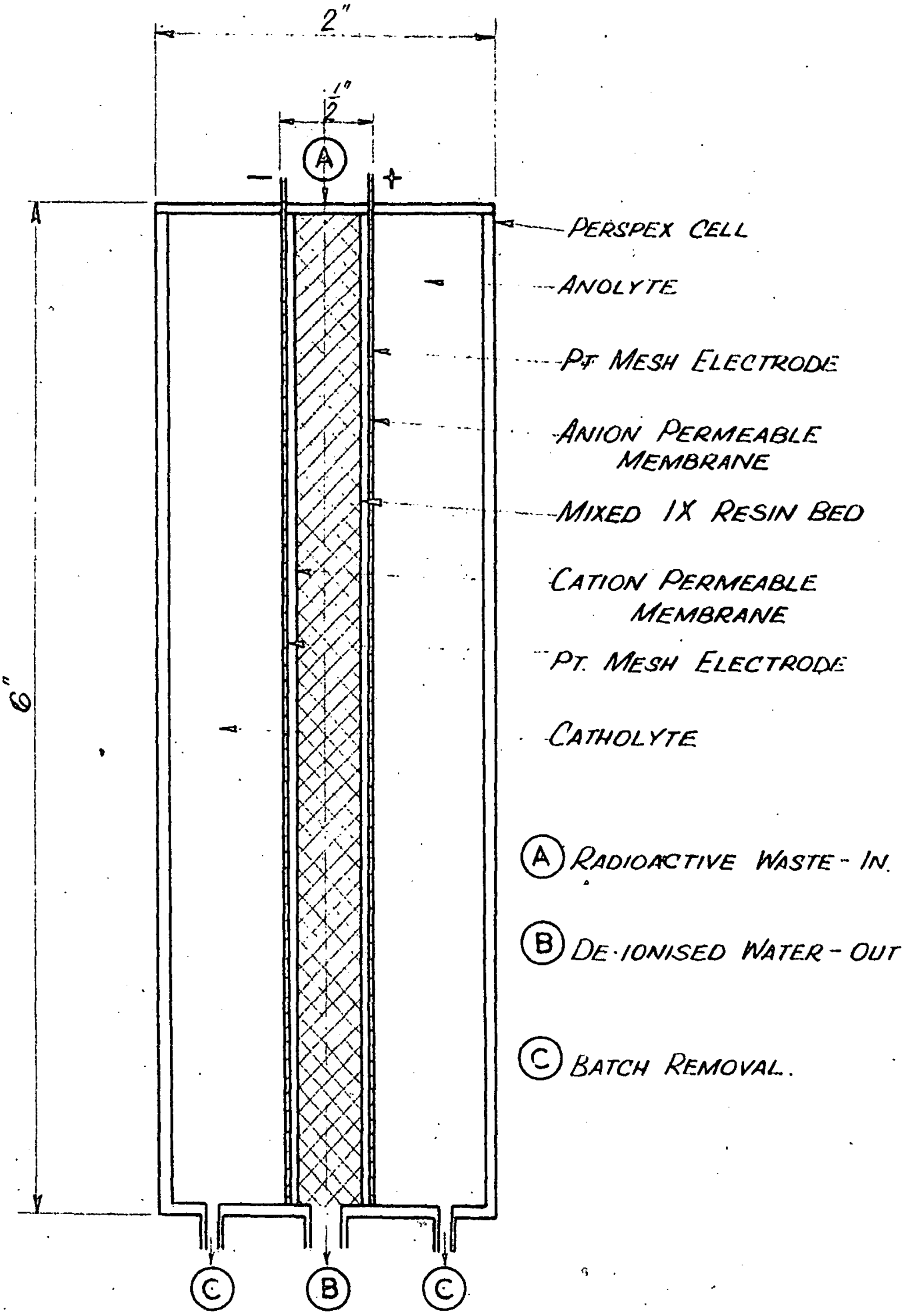
3.3 Graphite Technology (Mr. J.M. Hutcheon).

Mr. Hutcheon was conducting investigations into properties of graphite for reactor use. The main specifications for reactor graphite are density, electrical resistivity and to some extent chemical impurities. In general if the electrical resistivity is within prescribed limits then the amounts of impurities are likely to be low. Chemical limits prescribed for boron and vanadium are -

Boron	2 p.p.m.
Vanadium	10 p.p.m.

There is a danger of boron pickup during electrolysis if a high boron graphite is used as anode. This could presumably be avoided if pre-electrolysis were carried out to deplete the anode of boron.

Experimental test billets of graphite 4 inches diameter and 12 inches in length were produced in this section.



SECTION OF CELL

FIGURE- 4.

The usual raw materials are coke and coal tar pitch. The billets were extruded from a high pressure die after mixing of the raw material. Three furnaces were used during firing of the billets -

(1) Wire wound, up to 1000°C. This operates at an internal pressure of 200 p.s.i.g. The billets are sealed in a drum and packed in graphite dust at this stage. The internal pressure in the drum is kept at just below the 200 p.s.i.g. in the furnace to avoid leakage of volatiles and attack on the furnace windings.

(2) Molybdenum wound operating up to 1300°C. Cracked ammonia gas is used to protect the windings. A separate ammonia cracking plant is used to provide the nitrogen and hydrogen.

(3) A carbon resistance furnace using hairpin type carbon elements and operating up to 3000°C.

Mr. Hutcheon indicated that there would be some billets of impermeable graphite available. The test billets are 4 inches diameter and 12 inches in length. Some of these spare billets could probably be obtained on request.

3.4 Fission Product Technology Group (Head of Group - Dr. E. Glueckauf.)

3.4.1 Ion Exchange Membranes -

The group had been working on membrane cells for removal of low grade radioactive fission products from waste water. They were expecting to obtain from Permutit Ltd. a Pilot Scale cell for experimental purposes, but had not received it. A small cell had been operated successfully in the laboratory producing de-ionised water of conductivity grade. (Fig. 4).

The ion-permeable membranes act as barriers and the main de-ionizing is done by the mixed bed of resin contained between the membranes. The platinum mesh electrodes extend the full width and height of the cell. In practice a good deal of the impurities are removed by various chemical treatments and the cell is used for final stripping. The cell used was 6 inches high, 2 inches wide and one inch deep.

3.4.2 Inorganic Ion Exchange Materials -

Considerable progress had been made with the development and use of inorganic materials. Natural vermiculite had been used for cation removal, while attempts were made to aggregate clays such as montmorillonite for similar use. Organic resins will not stand the conditions of operations which involve temperatures up to 300°C. and pressures up to 1200 p.s.i.

It was found that various oxy compounds of some metals possess remarkable ion exchange properties, which persist under the conditions mentioned. The compounds studied most were zirconium phosphate and zirconium oxide. Thorium phosphate also exhibits ion exchange properties and in general, probably most metallic compounds of amphoteric nature will do so.

Zirconium phosphate is produced by precipitation from solution in a gelatinous form which is filtered and subsequently dried.

The cake acts much like gelatinous silica and breaks up into irregular fragments which are subsequently heated at temperatures not exceeding 200°C. A fairly coarse product results, with the majority of particles in the range − 20 + 100 mesh. The particles are stable at temperatures up to 300°C. and pressures of 1200 p.s.i. There are no undue attrition losses or lowering of capacity providing they are kept wet during the process.

Zirconium phosphate acts as an anion exchanger with capacities ranging from 1 − 5 milli-equivalents per gram depending on pH.

Zirconium oxide acts as an anion exchanger up to pH 8 but at high pH, about 13, becomes cationic.

Thorium phosphate will not remain aggregated but crumbles on drying. Its exchange capacity is lower than the zirconium compound but the exchange rate is about the same. Some experiments had been carried out with mixed Zr–Th phosphates and aggregates containing up to 80 percent thorium phosphate were made successfully.

A sample of zirconium phosphate "resin" had been obtained from a U.S.A. source. This was in bead form and had to be kept wet even when not in use. It was not known how the beads were produced, but the makers claimed an effective surface area of about 400 square metres per gram.

The mechanism of the ion exchange is thought to be similar to that of the synthetic resins with ZrO-Zr linkages and possibly PO_4H'' and $PO_4H_2^-$ groups present. Some form of polymerisation through cross linking is possible, but it is not yet possible to control the degree of "cross linking" on account of the fact that the material is all of one kind.

The investigations are only in early stages but a considerable programme is envisaged and it is understood that similar work is proceeding in U.S.A.

SECTION 3 .. OTHER ATOMIC ENERGY ESTABLISHMENTS.

1. SPRINGFIELDS.

1.1 Uranium Metal Production

The conventional plant using ether extraction, and conversion of oxide to UF_4 followed by calcium reduction to metal was still in operation and was the same in most respects as when seen by P. Dixon and R. Canning. Precipitation of uranium by hydrogen peroxide prior to solvent extraction had, in large measure been discontinued since most concentrates have only small amounts of boron which is easily removed in the solvent extraction (ether) step. In the final stage magnesium reduction of the UF_4 may replace calcium reduction. Before undergoing the final firing stage, the UF_4 is compacted in briquettes with magnesium metal.

A process for production of UF_4 was projected in which the concentrate was dissolved as usual and the uranium extracted by solvent extraction. The nature of the solvent was not disclosed but it was presumably tributylphosphate. Stripping and backwash follow before proceeding to ammonium-di-uranate etc.

1.2 Research & Development Springfields .. Chemical & Physical including Metallurgy

1.2.1 Thorium Extraction -

Several processes have been examined for the production of ThO_2 from monazite and "thorite".

Monazite is mainly Malayan (7% ThO_2, 58% Ln_2O_3) Nigerian (5% ThO_2) or Korean. There is also South African monazite rock containing other phosphate mineral, possibly apatite. This rock is not as amenable to conventional treatment as monazite but is the main raw material being used by Thorium Limited.

The "thorite" contains up to 50% ZrO_2 and the extractive properties of ThO_2 vary considerably. There is probably a large proportion of zircon in most samples.

There are two main routes to ThO_2 separation.

(1) Alkaline.

Leaching monazite with 50% NaOH w/v and filtration of insoluble hydroxides. The precipitated hydroxides are dissolved in acid and the ThO_2 reprecipitated at pH 5.5. Alternatively, the precipitated hydroxides may be leached with HNO_3 at constant pH 2.2 - 2.3 so as to dissolve the $Ln(OH)_3$ leaving $Th(OH)_4$ insoluble. Neither method is much favoured.

(2) Acid Leaching.

A process is being considered for recovery in an acid circuit as follows :-

Digestion of Monazite with concentrated H_2SO_4, 1 part of ore plus 2 parts of acid at 200°C for four hours. Thence several alternatives.

(a) The residue is leached with ten parts water to one part ore which dissolves 99 percent of the ThO_2 and most of the Ln_2O_3. The lanthanons can be removed at pH 0.6 by precipitation as double ammonium sulphates. It was claimed that the contamination with thorium was low in tests on a laboratory scale, but results were variable. Thorium could be recovered from the filtrate by alkaline precipitation, causticising etc. The more favoured method is solvent extraction of the HNO_3 solution of the hydroxide using tri-butylphosphate. Any uranium present was first extracted with 5% TBP-Xylene, and the thorium extracted with 40% TBP-xylene.

(b) The residue is leached with 4½ parts water to one part ore. Most of the thorium is dissolved but 2/3 of the lanthanons remain in the residue. It was suggested that washing of the residue might be deleted involving a loss of 5 - 10% ThO_2, in order to simplify the process.

The thorium is recovered from the liquor by precipitation as anhydrous $Th(SO_4)_2$. The liquor is added to concentrated H_2SO_4 at temperatures of (1) 120°C, (2) 200°C. The latter temperature gives a better recovery and better product but poses handling problems on a larger scale. The usual technique is to drip the leach liquor into the hot H_2SO_4.

The $Th(SO_4)_2$ is filtered, washed with concentrated H_2SO_4 and dissolved in water. The best temperature for dissolution is 45°C. $Th(OH)_4$ is precipitated at pH 6 by addition of NaOH or NH_4OH. This step could be done by direct dilution with water to give the required pH but would involve large volumes and difficult handling problems.

The products obtained usually contain very little phosphate.

The details of the solvent extraction procedure are included in a Research & Development Branch (Springfields) Report (3).

1.2.2 Niobium -

Two methods are being investigated on Pilot Scale.

(1) Dry Way.

Chlorination of ferroniobium (60% Nb-Ta) followed by condensation of the chlorides. The chlorides are distilled fractionally at about 220°C. so that Ta, Nb chlorides volatilise leaving $FeCl_3$ as a residue. The $TaCl_5$ is then distilled off leaving the $NbCl_5$ in solid form substantially free from impurities. The Nb metal is produced by a modified Kroll process by distillation into molten magnesium metal. The metal is of high purity and contains less than ½% oxygen.

(2) Wet Way.

Ferroniobium is decomposed by digestion with concentrated KOH solution followed by filtration etc. An insoluble sodium salt is then precipitated, filtered washed and treated with acid to produce mixed oxides of Ta and Nb. These are dissolved in HF and the Nb is recovered by crystallisation of K_2NbF_7. The K_2NbF_7 is suitably treated (dry) with metallic Na, (no details given), to produce metallic Nb.

1.2.3 Other aspects of Research & Development -

Work was proceeding on solvent extraction of uranium, details of which were not available. A type of micro air lift is used in mixer settler units of similar design to those used in the Chemistry Division at Harwell. The advantage of this system is that flow can be stopped at any time and the phases at each stage analysed. Edwards micro flow control valves are used to control flow which is produced by normal constant head gravity feed.

Refining of Uranium Metal :

A pilot scale cell has been built for testing the electrolytic refining of uranium. It is intended to use uranium metal as anode in a bath of $LiCl_2$-KCl eutectic with a molybdenum cathode. The eutectic will be heated internally by 3 carbon electrodes operating on A.C.

1.3 Reactor Research at Windscale (Sellafield)

The various rigs used for liquid sodium metal cooling were inspected and problems associated with its use were explained. Magnetic pumps are used to pump the liquid metal. Pumping efficiencies range up to 50 percent.

Some fission product disposal methods were explained during a tour of some of the laboratories. Solvent extraction experiments were proceeding but details were not disclosed. In these experiments some extraction cells were built from solid perspex blocks drilled appropriately to form mixer settler units. Stirring was by single rods and the mechanisms were coupled to a crown wheel and pinion system by flexible drives.

1.4 Uranium Metal Production and Fabrication

Observations made at Harwell, Springfields and Windscale emphasised the magnitude of the task of production of uranium metal and fuel elements. Apart from problems of production and fabrication there are complex problems associated with the physical state and behaviour of fuel elements. There are considerable numbers of staff working on physical and metallurgical aspects at Springfields and Windscale. The problems include bursting of "cans" and wrinkling, which can be very serious.

The physical phase changes are not well understood and the amount of technical equipment and staff required to pursue these problems would be enormous by S.A. standards.

It would be desirable for a very careful assessment to be made of such problems before considering the establishment of a reactor especially if production of fuel elements were considered.

In fact the whole question of metal production should be studied from the viewpoint of economy and disposal since it is unlikely that a market would be available outside Australia.

The general opinion expressed by technical and administrative personnel who are aware of these problems, is that South Australia would be advised not to enter the field of fuel production and technology.

SECTION 4 .. CHEMICAL RESEARCH LABORATORY, TEDDINGTON.

1. INORGANIC SECTION.

1.1 Rare Earth Fractionation by Ion Exchange

Three methods are generally applied to separation of lanthanons on cation exchange resin.

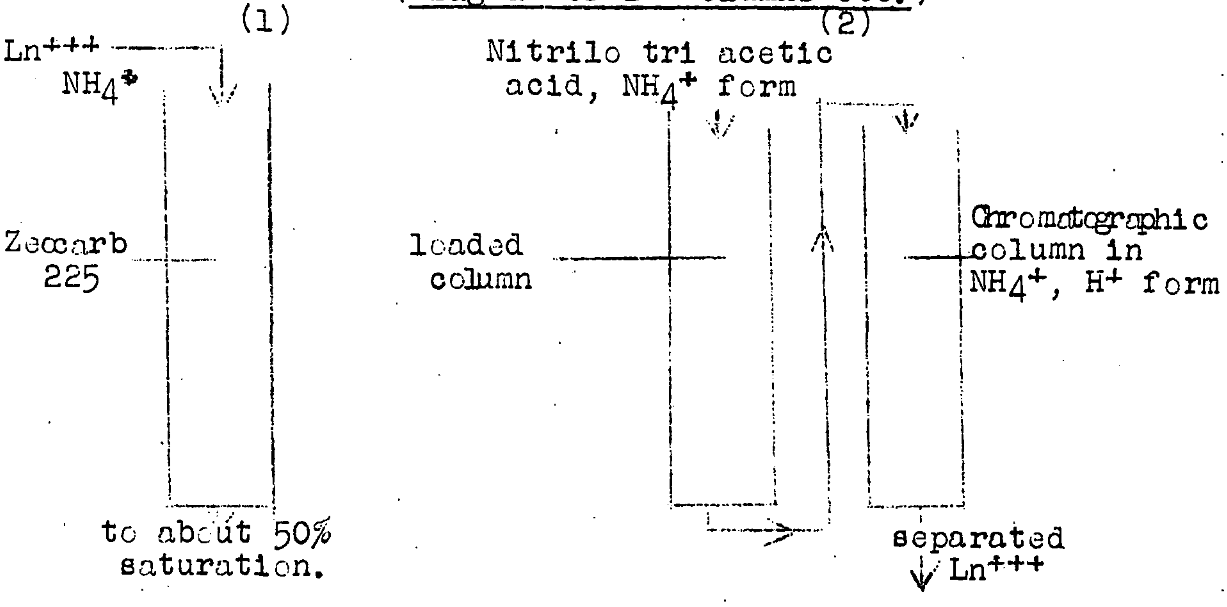
(1) The resin is loaded to saturation with a solution containing lanthanons and eluted with citrate solutions at controlled pH. This was an earlier method and gave eluates with very low concentrations of lanthanons.

(2) The loaded column is eluted with ethylene-diamine-tetra-acetic acid and the eluate is passed through a column containing copper following the lanthanon column. This method was developed by Spedding and other workers in the U.S.A., and depends on improved fractionation due to presence of copper on the second column. The members of the section were not interested greatly in this process and did not have any explanation of the mechanism.

(3) The only method being investigated at C.R.L. is as follows :-

> Lanthanons in chloride solution are loaded on a cation resin, specifically Zeocarb 225 to about 50 percent capacity. The remainder of the capacity is occupied by NH_4^+.
>
> The loaded resin is eluted with nitrilo-triacetate (NH_4 form). The eluate is passed through a second column in which the ratio of NH_4^+/H^+ on the resin is varied by prior treatment. Fairly good separations are obtained of the "light group", particularly Nd, Sm, Pr, but some difficulty is being experienced with the "heavy group".

(Diagram of IX Columns etc.)



The section was currently interested in recovery of Tm from lanthanon residues using this method. The lanthanon residues contain three parts Tm/1000 Ln_2O_3. Flow rate of eluent was about ½ cm/min. or 600 ml/hr. on 2 inch columns.

1.2 Rare Metals Recovery

A group in this section was working on recovery and purification of rare metals, germanium, gallium, selenium, etc.

In the past, coals from Australia had been examined for germanium and other elements but nothing of importance had been found.

Selenium which can be present in sulphides, notably pyrite, is generally recovered from the dilute acid wash stage after solids removal from flash roaster gases in contact acid plants. Metallic Se is deposited by reduction at this stage.

Some products contain up to 80 percent selenium. The world supply is short and with the demand increasing, it is expected that the price will rise.

An intensive survey of possible South Australian sources seems justified at an early date. The present demand is for (1) rectifiers, (2) glass manufacture.

1.3 Purification of Metals

Considerable work has been done on purification of low melting point metals by zone melting in pyrex glass tubes sealed in vacuum. Metals such as bismuth, selenium and tin in a high state of purity are sealed off in tubes in vacuum and melted by moving a small hot zone along the tube. In the laboratory, movement rates of about 0.5 cm/hr are employed, the heating zone being ½-1 inch long. Several ingenious devices are used to make the operation simple and automatic. The main requirements are low horse power motion and a variety of ordinary "Meccano" parts and gears. The segregation of impurities at the end of the bars of metal can be clearly seen in test pieces.

The technique is also applied to salts - e.g., indium chloride and organic compounds. For successful operation of zone melting it is essential that the impurities present should cause either lowering or raising of the melting point of the solid.

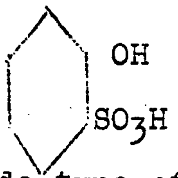
2. HIGH POLYMERS SECTION.

2.1 Preparation of Resin

The reaction kinetics of synthetic resins prepared in this section were being studied. The resins are prepared by adding various proportions of di-vinyl benzene to polystyrene and cross linking by polymerising with benzoyl peroxide. A proprietary line "Promulsin" is used as a suspending agent for the resin. This is most likely a carboxy methyl cellulose derivative. Studies included the effect of varying the number of exchange sites and the amount of swelling of resin due to water.

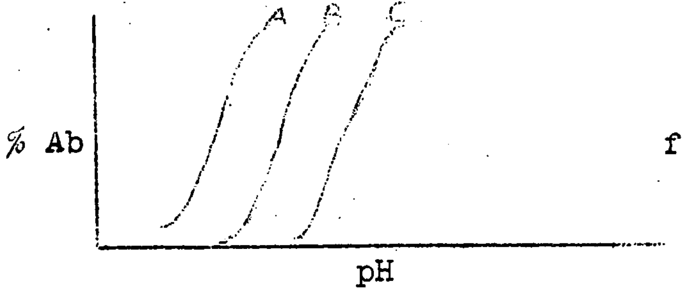
Ions used so far in studies of resin behaviour have been simple, i.e. Na^+, K^+, NO_3', Cl'.

Investigations have shown that substituted groups such as $COOH'$, OH, give greater selectivity for some metals than ordinary cross linked polystyrene resins, i.e. resins of the form -



Thus the phenol formaldehyde type of resin may be more efficient in some cases.

Some work had been done on condensing polystyrene resins with complexing agents such as EDTA to give greater selectivity for metals with variation of pH. Absorption curves are of the type.



for say 3 metals
A, B, C.

2.2 Ion Exchange Membranes

A good deal of the work was with ion exchange membranes of the type IRA 400, zeocarb 225. Polyethylene was used as a binder and usually comprised about 50 percent of the membrane. It had been found that good electrical conductivity was obtained with most membranes when wet. This is thought to be due to swelling of the resin allowing small pockets of electrolyte to enter interstices between resin and binder.

Homogeneous resin sheets have not been much studied owing to fragility.

2.3 Chromatographic cellulose is prepared by mixing cellulose powder and fine resin and grinding together (5). The product is formed into sheets and allowed to dry. The RF factor of some metals is improved and more clear cut separation is possible, e.g. cobalt and nickel. This may be a method for spot testing for uranium in liquors if a cation exchange resin were mixed with cellulose and a nitric acid-ethyl acetate extraction used. The ferric iron may be further retarded.

3. RADIOCHEMICAL GROUP.

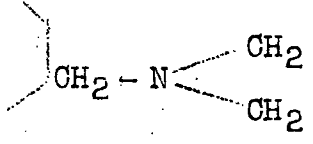
3.1 Ion Exchange

3.1.1 Recovery of Gold –

The recovery of gold from conventional cyanide solutions has been investigated. A typical cyanide solution contains :-

Au 6 ppm, Ni 40, Cu 30, Fe 24,

in solution of 150 mg. NaCN/l. Investigations starting with Deacidite H showed that resins containing a mixture of weak and strong base groups have good selectivity for Au. A typical resin has 6 – 10 percent strong base containing quarternary ammonium groups and 90 percent weak base with groups of the type benzyl dimethyl amine.



Typical absorption curves show break through of Fe, Cu, Ni, in that order up to say 25 l. Whereas break through for Au is at say 250 l.

The resin is eluted with NaCNS at about 0.2 N and the Au is recovered from the eluate by electrolysis. The stripped eluate is recycled without necessity for bleed off. Recovery of Au from cyanide solutions is 97.7 percent.

The resin base used for these experiments is chlormethylated polystyrene.

3.1.2 Resin in Pulp -

Investigations were in progress for the recovery of uranium from Mary Kathleen leach pulp. The Ion Exchange resin was used in the form of blocks which were moved along a trough counter current to the pulp. Fresh blocks were introduced at the end opposite to the point of introduction of the pregnant pulp. The loaded blocks were removed as they reached the other end of the trough and washed and eluted. No results were forthcoming but it was claimed that the system showed promise.

3.2 Solvent Extraction of Uranium

Work had been continued on the use of various alkyl phosphate esters for the extraction of uranium from sulphate solutions. Much of the work had paralleled work all ready carried out in the Research & Development Laboratories in Adelaide and many of the conclusions arrived at were similar. The most satisfactory reagent appeared to be di-2-ethyl hexyl phosphoric acid as used in Canada and the United States. It had been found that successful differential extraction of uranium could be obtained by limiting the contact time of the solvent (in kerosene solution) and the aqueous phase, to around 1 - 2 seconds. By this means a satisfactory recovery of uranium could be obtained while ferric iron and other impurities were not extracted. Again no actual details were available but there is no doubt that it should be possible to apply such a system to Australian ores if the necessity arose.

3.3 Analytical

3.3.1 Thorium

Thorium was determined in monazite or thorite containing zirconium by a cellulose column - volumetric or colorimetric procedure. The sample of ore or mineral was fused in KOH and the HNO_3 solution of the melt was evaporated to dryness. The residue was treated with reagents as follows:

20 ml. 25% V/V HNO_3
H_2O_2 was added to reduce Ce^{iv} to Ce^{iii}
8 g. $Fe(NO_3)$ hydrated.
1.4 g. Na_2HPO_4

The bulk of the zirconium was precipitated as phosphate and the excess phosphate was complexed by the ferric iron. The mixture was adsorbed on a wad of activated alumina and transferred to a cellulose column which contained a layer of alumina above the cellulose. The column was eluted with ether containing 12½ percent V/V HNO_3. Thorium was determined in the eluate subsequently either by precipitation as oxalate or titration with EDTA* using Alizarin Red S and methylene blue as indicators. The colorimetric method with "Thorin" had also been used.

<u>Note</u> - At Springfields Thorium was separated from zirconium by precipitation as fluoride and subsequent solvent extraction by TBP in HNO_3 solution.

<u>3.3.2</u> Uranium -

The colorimetric procedure of De Sesa and Nietzel (6) had been investigated. This was a modification of previously published work on the measurement of the absorbance of uranium-thiocyanate complex in acetone solution.

At C.R.L., a solution of 2 acetone/1 water was used for optimum colour development. It was found that satisfactory results were obtained for liquors if the stannous chloride and ammonium thiocyanate solutions were kept in separate containers and not mixed as suggested by De Sesa and Nietzel.

* ethylene diamine tetra acetic acid.

SECTION 5 .. OTHER ESTABLISHMENTS VISITED.

1. THE IMPERIAL COLLEGE (London University).

1.1 Royal School of Mines

Several visits were made to the mineral dressing laboratories. The equipment and procedures used were mainly conventional. One section was investigating pressure leaching of minerals under alkaline conditions.

The process used is subject to patent application and no details were available. It was however, apparent that leaching was carried out with either NaOH or KOH under controlled conditions.

The process had been applied to the recovery of soluble zirconium salts from the mineral zircon. It was also claimed that tantalum and niobium salts could be recovered from tantalite and columbite. The mechanism of the leach is probably the effect of alkaline hydroxide at high temperature (200°C). Natural steam pressure only was used except where there was a pressure drop due to withdrawal of samples. In this case the pressure was maintained by introduction of nitrogen.

A stainless steel autoclave had been used with a conventional lid and gland stirrer, but it was intended to build a model which contained the stirring mechanism in the lid. It was hoped that by so doing, the usual troubles attending the use of gland stirrers would be overcome.

2. THE FULMER RESEARCH INSTITUTE.

The Institute is situated in ideal rural surroundings at Stoke Poges about 20 miles from London. The laboratories contain mostly physical and physical chemistry equipment and the work carried out has been mostly in these categories. X-ray diffraction and electron microscopy are included in the activities while there is a small analytical section to cope with chemical requirements.

The research work is sponsored by various organisations concerned with metals production and fabrication and consequently much of the work is of a confidential nature.

Considerable progress had been made in research into metals production by a group headed by Dr. Gross. Dr. Gross has been responsible for investigating the production of metals by a process involving disproportionation of gaseous chlorides under established conditions (7), (8). Metallic aluminium of high purity has been produced using Fe-Al alloy as the starting point and $AlCl_3$ as the vapourising medium.

$$2\ Al + AlCl_3 = 3\ Al\ Cl$$

The resulting vapour mixture reverts on cooling, forming Al and $AlCl_3$ the latter being recycled. It was considered likely that the process would work satisfactorily if the starting material were an alloy of Fe-Al-Si such as could be derived from siliceous bauxites or clays.

The process had been applied successfully to the recovery of Ti from Fe-Ti. The reactions involved are believed to be broadly as follows :

$$\begin{matrix}\text{Fe-Ti} \\ \text{alloy}\end{matrix} + TiCl_4 \xrightarrow{?600-700^{\circ}C} TiCl_2 + TiCl_3 \quad \ldots\ldots \quad (1)$$

$$Ti\ Cl_2 + 2\ TiCl_3 \xrightarrow{1300^{\circ}C} Ti + 2\ TiCl_4(\text{recycle}).(2)$$

The $TiCl_2$ produced is a purple-black crystalline solid. It was necessary to sublime the mixed subchlorides in stage (1) and subsequently reheat to 1300°C to achieve stage (2), whereas in the production of Al the process was continuous.

The Ti metal was obtained in the form of a sponge which was subsequently remelted by an arc melting process. It was claimed that the measured "hardness" was lower than that produced by the Kroll process, indicating a higher degree of purity.

One of the problems associated with production of Ti was the supply of suitable materials for containing the reaction products. Owing to the extreme reactivity of Ti metal, there are few materials which remain unattacked especially at high temperatures. Investigation on these lines was proceeding using a 2 inch diameter mullite tube furnace wound with Pt wire for heating purposes. Inserts of various materials were used in the furnace to investigate their properties. The materials used included -

"Kromite" - a high Ni-Cr alloy

Graphite - various types were under investigation to determine the resistance to attack by titanium at temperatures up to 1300°C.

The work on metals included the determination of heats of formation of various metal chlorides. For this purpose, suitable apparatus was designed for each particular determination and the results obtained were claimed to be of a high degree of accuracy. Typical examples were the determination of H.O.F. of $TiCl_4$ (9) $TiBr_4$ and $ZrCl_4$.

Whenever possible, the experimental approach to problems is preceded by consideration of the thermodynamic equilibria involved and from this, much preliminary useful information is obtained.

The Institute is prepared to accept research staff from other organisations for limited periods to enable them to gain experience in particular fields of research. At the time of visiting the laboratories, a number of officers from Commonwealth Departments had been attached to the Institute. It is understood that officers from S.A. would be accepted under similar terms and it would be an advantage if arrangements could be made for some of the younger members to be sent to the Institute for experience.

3. THE THERMAL SYNDICATE WORKS, NEWCASTLE-ON-TYNE.

A visit was made to the Sales Department and factory of the Thermal Syndicate Ltd. to discuss requirements for silica laboratory equipment and to inspect the production procedures. The silica in the form of pure sand is heated to a working temperature of 1750°C in electric furnaces and fabricated according to the type of product required. There is little or no mechanical control of processes and most of the fabrication is carried out according to experience of the operators. This industry is definitely one in which personal experience is valuable and the loss of the services of a skilled operator is considered serious.

The company kindly supplied a copy of notes on the working of fused silica which will be incorporated in a brochure "about Vitreosil". The notes are included in this report in Appendix 2.

SECTION 6 .. VISITS OUTSIDE THE UNITED KINGDOM.

1. THE DEGUSSA CO. DEPARTMENT "DEGUSSIT".

The properties of ceramic materials were discussed with members of the Technical Staff of the "Degussit" works in Frankfurt, Germany. The ceramics produced by this organisation were mainly made from oxide materials. These would stand high temperatures but were not generally resistant to thermal shock and were in addition too expensive for general use. A small quantity of "Alsint" fused alumina ware was ordered for testing its suitability for fused salt work.

2. THE HALDENWANGE PORCELAIN WORKS, BERLIN.

Discussions were held with the sales and Technical staff at the Works and Laboratory premises at Spandau, Berlin. The persons taking part in the discussions were extremely helpful and spared no effort to be of assistance. The members of the Research Staff carried out tests to determine the permeability of various products to fused salt mixtures. As a result of the discussions it was decided that the material known as "Pythagoras", which consisted of 60% Al_2O_3 and 40% SiO_2, was likely to be satisfactory for the purpose intended. It was emphasised that the material was not highly resistant to thermal shock but that it should otherwise prove satisfactory providing that sudden temperature changes were avoided.

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APPENDIX I.

CONTROL OF CHLORINATION IN THE GIBSON PROCESS FOR URANIUM METAL

by

R.G. Canning [*]

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 easy hydrolysis of the solution indicated the presence of uranous oxy-chloride. This salt was unfortunately 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.

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[*] R.D. Report in preparation.

2.3 X-ray diffraction spectrometry of the solid samples

One series of six samples was examined in the Mineralogical Section, using 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 through stages 1, 2 and 3, could clearly be followed by the appearance of the solutions, 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.

Solution A — Uranyl chloride (UO_2Cl_2), containing

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

Approximately 0.1N free acid.

Solution B — Uranous chloride (UCl_4),

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 reoxidised to UCl_4.

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

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 by peroxidising reduced solutions that the correct end-point could be determined. 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 1.

TABLE 1.
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 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 1 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.

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APPENDIX II.

NOTES ON THE WORKING OF FUSED SILICA SUPPLIED BY THE THERMAL SYNDICATE LTD.

Two operations likely to be of interest to users of our material, e.g. for repairs, are cutting and fusing with the blowpipe and the following suggestions are given.

Cutting :

Tubes of reasonable length and up to 7/16" external diameter may be snap cut, that is a file scratch is made on the surface of the tube which is then snapped with the fingers as for glass. Sharp edges may be rubbed off on an abrasive wheel or stone. This is satisfactory for occasional use.

If many tubes are to be cut to length, or in the case of larger tubes and pipes of all sizes, then silicon carbide cutting wheels are used. Suitable wheels may be obtained from the Turrent Grinding Wheel Company or The Carborundum Company and when ordering they should be specified as being required for cutting fused silica. The usual dimensions are 6½" diameter by 1/16 to 3/32" thick, the latter thickness is usually for shaft drive. The wheel is used on a rotary cutting head running at a peripheral speed of 6000 ft. per minute. It is important that during the whole operation there should be a copious flow of water directed on to the cutting point.

The assembly used for this work simply consists of an electric motor fitted with a suitable flexible assembly to which the cutting head, with water supply arrangement and protection shield, are fitted. The water supply is conveniently arranged by leading a rubber hose from a tap to a metal tube fastening on to apart of the shield, which in turn is merely a semi-circular metal cover over the wheel.

It will readily be understood that the cutting assembly can be arranged for permanent mounting with flexible drive when required. Copper or phosphor bronze bonded diamond cutting wheels are also used where the volume of work justifies the expense. The speed should be similar to that used for silicon carbide wheels.

Tubes are cut by first grooving all round, then at three or four points around the periphery cuts are made right through the wall to leave a series of spokes which hold the parts together until they are finally cut away carefully to separate the two parts. The cut ends are then dressed on the side of the wheel.

The drilling of holes is a trepanning operation, as with glass, and either copper tube drills in association with silicon carbide abrasive, or "Habib' diamond drills (Impregnated Diamond Products Ltd.) can be used. The latter are well worthwhile if the volume of work justifies the expense. In all cases copious cooling water at the cutting point is essential. The drilling action is the application of light pressure with alternate 'press and lift', to enable debris to be removed by water. To avoid breakage at the back surface, drilling is performed from both sides or a glass plate is waxed behind the fused silica plate and the work suitably supported.

<u>Fusing</u>:

In all fusing work protective spectacles must be worn by the operator and the recommended glass is green 'Protex' grade 'C', $\frac{1}{8}$" thick (Chance Bros.) to give the best protection. British Standard 679 is the guide to this type of protection.

It is true that occasional repair jobs can be performed with an oxy-acetylene torch, but this is not recommended; oxy-hydrogen, oxy-coal gas and oxy-propane flames are preferable.

The following torches are recommended :

(a) For very small work, use British Oxygen Co.'s No. 35069 lead welding type torch fitted with hose protectors and having the injector hole drilled to 1/32" dia. This blowpipe may be used with oxy-hydrogen or oxy-propane, but not oxy-coal gas unless the gas supply is above 6" W.G. pressure.

(b) For small work use British Oxygen Co.'s No. 109616 lead welding type torch fitted with hose protectors and having the injector hole drilled to 1 mm. dia. This blowpipe may be used with oxy-hydrogen or oxy-propane, but not oxy-coal gas unless the gas supply is above 6" W.G. pressure. Beside being used as a hand torch, this unit may be mounted on a bench for working transparent tubing up to 1$\frac{1}{2}$" bore or translucent tubing up to 1" bore. Fused silica is not usually removed from the flame during blowing, so a light rubber blowing tube having a glass mouthpiece is used by the operator.

(c) For larger work, particularly the repair and joining of translucent tubes, coils and pipes, use C.S. Milne and Co. London Ltd., general welding torch injector model. This is supplied with heads, ejectors and nozzles in varying sizes according to the type of work to be carried out, and it is a valuable general purpose blowpipe. We use No. GL8 and GL10 heads and injectors with No. 8, 10 and 12 nozzles.

Usually oxy-coal gas is used with this torch but certain heavy work is best carried out with an oxy-propane (Pyro gas) flame, which is hotter and quickens the operation. Strain in the area around the joint is thus reduced.

Cleanliness is most essential in all fusion work and special instructions have been compiled for preparing transparent material.

For hand work the usual rotation in the flame is employed to ensure even heating. A suitable poker for belling or flanging an open end consists of a 12" length of 3/16" nickel chrome wire. More elaborate quartz blowing necessitates special graphite shapes which can be attached to the end of the poker for tooling the work. The joining and repairing of translucent fused silica pieces which are usually of larger size call for special mention. For example, tubes and coils up to 3" bore and wall thickness up to ¼" can readily be welded. The ends to be joined are first ground to knife edges to form a V shaped notch all around when butted together, the knife edges being on the inside periphery. These edges are joined after adequate preheating by first using a fused silica filling rod of 3/16" dia. drawn down to ⅛" at the tip. The blowpipe flame is directed into the notch and on to the end of the rod at the same time.

When the end of the rod is sufficiently plastic, it is pressed right into the base of the Notch and pulled so that the drawn end is maintained, this procedure is repeated progressively until the whole joint is completed. The welding operation must be done expeditiously, maintaining the heat all round the joint by constant flame manipulation. The finished work is then annealed in a furnace, operation being at 1050°C for an hour to remove bulk strain from the area around the joint. If it is not possible to place any article in an annealing furnace, a construction of firebricks around the joint and suitably mounted welding torches may suffice.

While the skilful operator may successfully anneal joints up to 2" external dia. with the general welding torch, the furnace method is essential for larger work.

The methods described above can be applied within certain limits, to the welding of large sections up to ca. 6" bore. It has been mentioned earlier that in general parts for chemical plant above 3" bore have a wall thickness of $\frac{3}{8}$" rising to $\frac{3}{4}$" in the largest sizes and it is, therefore, necessary to grind the walls down to $\frac{1}{4}$" for some distance before cutting the knife edges which are to form the V-notch for filling at the joint.

There are more risks of breakage in making the large welds, which in turn raise the problem of adequate annealing.

This is why many repair jobs are declined, e.g. broken sockets on pipes are not usually repairable. Cost of repair, allowing for risk of breakage must always be balanced against renewal cost.

During manufacture, special moulding methods are used when, e.g. branches are to be attached to larger pieces. In such a case a boss is first blown on the moulding, it is then cut away to give a suitable nozzle to which a branch may be attached. In this way the desired thin wall for the junction is more easily obtained, and there is less chance of the torch flame impinging on the main body to increase the risk of strain. Additionally, graphite plate baffles are used to protect the main body from the blowpipe flame.