

# RADIOCHEMISTRY AT HARWELL FROM 1946

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# STRUCTURE OF TALK

- The start of chemistry at Harwell.
- Design and construction of B220.
- Reprocessing and plutonium
- Radioactive elements.
- Reactor fuels.
- Radioactive waste disposal.

Note that a very selective approach has been adopted in preparing this talk.

# BACKGROUND

- Decision to establish Atomic Energy Research Establishment, at RAF Harwell Berkshire, 1945.
- “ to set up a research and experimental establishment covering all aspects of the use of atomic energy”
- Site open from 1<sup>st</sup> January 1946

# CHEMICAL PROBLEMS ASSOCIATED WITH NUCLEAR POWER

- Uranium purification and enrichment.
- Uranium and plutonium fuels.
- Reprocessing and plutonium preparation.
- Fuel performance, under normal operation and accident conditions.
- Reactor coolant.
- Radioactive waste treatment and disposal.
- Actinide, fission product and other radioactive element chemistry.
- Analysis.

# EARLY WORK

- Chalk River, Canada. Early work on irradiated fuel reprocessing. Trace quantities of plutonium available.
- Urgent need to produce data for production plants at Windscale (now Sellafield).
- Reactor development for civil purposes.

# B220 SPECIFICATION

- Objective “ To provide facilities for safe chemical treatment on a laboratory scale, of radio-active material which cannot be conveniently dealt with in the ordinary chemical laboratories”

# B220 DESIGN

- Separate wings for alpha and beta/gamma work.
- “Building of fireproof construction throughout.”
- “Smooth easily cleaned interior surface, free from cracks and crannies ....”
- “Plastic wall and floor coverings which can easily be removed when contaminated.....”
- “Dr Pontecorvo agreed that services and ducts should be above corridors and laboratories.”
- Minimum of 7 fume cupboards per laboratory.  
“Fittings to be stainless steel or chrome plated.”

# B220 DESIGN

- 6-10 air changes per hour for laboratories, 30-60 changes for fume cupboards.
- Ventilation plant 120 m<sup>3</sup>/sec.
- Electrostatic precipitators.
- 2500m ventilation trunking, up to 5m by 5m.
- Liquid effluents discharged via delay tanks, four pairs of 25,000 gallons each.

# REPROCESSING

- Initial work at Chalk River, Canada, continued at Harwel.
- Butex , dibutyl carbitol selected as solvent for extraction of Pu and U from nitric acid solution.
- $C_4H_9.O.C_2H_4.O.C_2H_4.O.C_4H_9$
- Packed columns for extraction
- Very high decontamination factors from fission products and other impurities,  $DF > 10^8$ .
- Studies of chemistry of fission products such as Ru.

# REPROCESSING

- Waste Management influenced choice of Butex; fission product wastes could be evaporated to small volume .
- $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  “most dangerous components”.
- “Even if the Cs and Sr cannot all be sold it has been shown that they can be adsorbed on special clays which can be baked so as to render them insoluble. The baked radioactive clay can then be safely buried in the ground.”
- Spence 1956.

# REPROCESSING

- Tributylphosphate in kerosene dominated later studies.
- Increased emphasis on minimising effluents and behaviour of longer lived nuclides such as  $^{237}\text{Np}$  and  $^{99}\text{Tc}$ .
- Chemistry relevant to fast reactor reprocessing e.g. 100 day cooled fuel, concentrated Pu solution chemistry.

# PLUTONIUM METAL PREPARATION

- Saturday evening, December 1951.
- Small quantities available for trials.
- Utilised large fixed glove boxes, “shop windows”. Two rows of floor to ceiling glove boxes with a pressurised suit area between the rows.

# PLUTONIUM METAL

- “When it had been safely wrapped in a polythene bag it was passed from hand to hand so that people could feel its radioactive warmth.”
- First weapon test October 1952, materials fabricated at Aldermaston..

# PLUTONIUM METAL PROPERTIES.

- Five allotropic forms.
- Properties published in Nature March 1954 “following a recent declassification decision”.
- “Full discussion of the theoretical implications will become possible only when security limitations permit the disclosure of some other properties of plutonium.”

# RADIOACTIVE ELEMENTS

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- “about 14 new or virtually new elements have been made available for chemical investigation since 1939, making perhaps the greatest accession to inorganic chemistry for over fifty years” (Spence)
- Spence ensured that high purity stocks of radioactive elements were available.
- Major studies in B220 on Po, Pa, Pu, Np, Am and many others.

# POLONIUM

- Prepared by irradiation of Bismuth.
- Milligram quantities available for study.  
Activity 4.5 Ci/mg.
- Double skinned glove boxes. Containment of Po within glove box as far as possible.
- 30 plus compounds prepared and characterised.

# PROTACTINIUM

- Separated from uranium production wastes.
- 60 te sludge from uranium purification processed to give 125g Pa.
- Extensive studies on chemistry.
- Preparation of Pa metal by modified van Arkel technique.
- PaC and small quantity of  $I_2$  heated to give volatile  $PaI_4$  and  $PaI_5$  which are decomposed on a hot tungsten filament to give Pa metal plus  $I_2$ .

# URANIUM FROM SEA WATER

- Uranium ca 3 ppb in sea water as a U(VI) carbonate complex. ( $4.2 \times 10^9$  tonne)
- Removal by titanium hydroxide, uptake of 300 micro g/g, and elution with sodium carbonate solution.
- A project ahead of need???

# URANIUM OXIDE CHEMISTRY.

- Fundamental studies on  $\text{UO}_x$  system.
- Early emphasis on preparation of fuel grade materials and fundamental properties.
- Studies extended to  $(\text{U,Pu})\text{O}_2$  and carbide systems.

# FAST REACTOR FUEL

- Mixed uranium plutonium oxide.
- Made by milling  $\text{UO}_2$  and  $\text{PuO}_2$  together followed by, granulating, pelleting, high temperature sintering and grinding to size.
- Dusty, dose intensive process.

# GEL PRECIPITATION

- Mixed uranium/plutonium nitrate solutions plus additives formed into spherical droplets by pumping solution through a vibrating jet.
- Hydrated oxides precipitated in ammonia solution.
- Dried.
- Sintered at high temperature to high density.
- Dust free process and product.

# HIGH TEMPERATURE STUDIES IRRADIATED URANIUM

- Safety assessments required data on fission product release from  $\text{UO}_2$  and  $\text{UO}_2/\text{PuO}_2$  fuel.
- Failed fuel and accident conditions simulated.
- Releases quantified using thermal gradient tubes.

# RADIOACTIVE WASTE DISPOSAL

- From early 1980s focus on disposal of waste in cemented waste forms to deep underground repository.
- Need to quantify and understand chemical behaviour of long lived radionuclides such as U, Np, Pu, under reducing, high pH conditions.
- Cement provides chemical barriers to radionuclide migration through solubility limits and sorption.

# COMPLEXING AGENTS

- Some wastes contain cellulose, which degrades under alkaline conditions.
- Iso -saccharinic acid (ISA) degradation product can complex with plutonium and enhance solubility .
- $\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2.\text{C}(\text{CH}_2\text{OH})\text{OH}.\text{CO}_2\text{H}$

# SORPTION ON CEMENT BACKFILL

DISTRIBUTION RATIO  $R_d$ ,  $\text{cm}^3/\text{g}$

$R_d$  = concentration of radionuclide in solid/concentration in solution.

I 10

Tc 6,000

U(IV) 8,000

Np 60,000

Pu 50,000

From NSS/R277

# CONCLUSIONS

- B220 at Harwell was the first advanced radiochemistry building in the UK.
- Harwell took forward the chemistry of many radioactive elements.
- Harwell provided the basic chemistry to underpin the UK civil nuclear industry.