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# Polymer Challenges in Waste Management

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# Introduction

- Jacobs provide professional, technical, and construction services operating across 40+ countries with 60,000 employees.
- We offer a specialist radiation materials consultancy supported by our Co-60 gamma irradiation facility.
- We support many clients from across UK and Europe working across multiple sectors including nuclear, space and defence.
- We offer experimental irradiation services – testing to required standards or designing tailored approaches.
- Our services include programme management, experimental design and operation, measurement, analysis and modelling.

# Polymeric Encapsulants

# Case Study 1 - Polymers as Waste Encapsulants

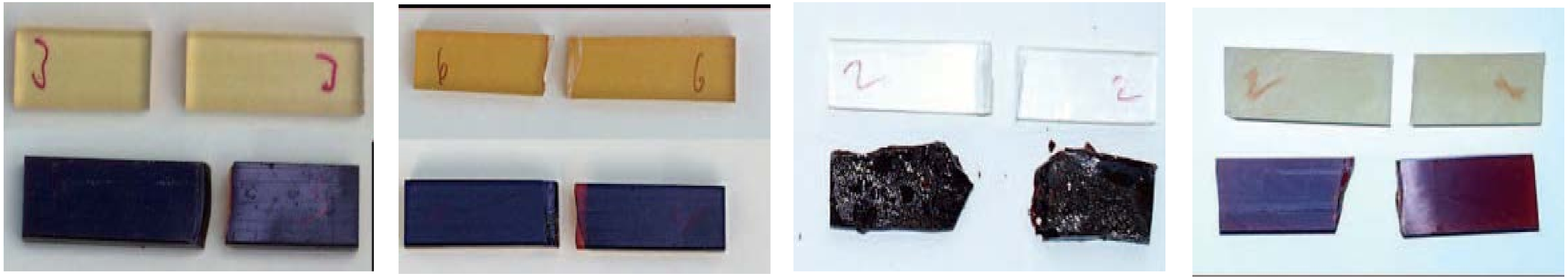
- The most common approach to immobilising nuclear waste is to encapsulate in a cementitious matrix using a multi-barrier approach.
- Cementitious materials are not appropriate for all waste types. For example, reaction between chemically active metals and the grout can lead to enhanced corrosion of the wasteform and compromise long-term performance.
- Alternative encapsulant materials may be used for niche wasteforms e.g. organic polymeric materials such as vinyl ester styrene (VES) and epoxy resins.
- Research has been carried out to explore long-term suitability of polymers for use as waste encapsulants. Jacobs has characterised the effects of radiation, thermal ageing and aqueous environments on the long-term stability of polymer encapsulants.

# Ageing Conditions

- Irradiations carried out on samples at dose rates of ~ 3 kGy $hr^{-1}$ up to a total dose of 10 MGy. Further studies at lower dose rates were also carried out to assess potential for dose rate effects.
- Changes in material properties assessed using the following techniques:
  - Flexural and compressive strength testing
  - Gel-fraction measurement
  - Fourier Transform Infrared Spectroscopy (FTIR)
  - Gas evolution
  - Leach rates
    - Total organic Carbon (TOC)
    - GC-MS for organic volatiles
    - Ion chromatography (chloride)

# Results - Observations

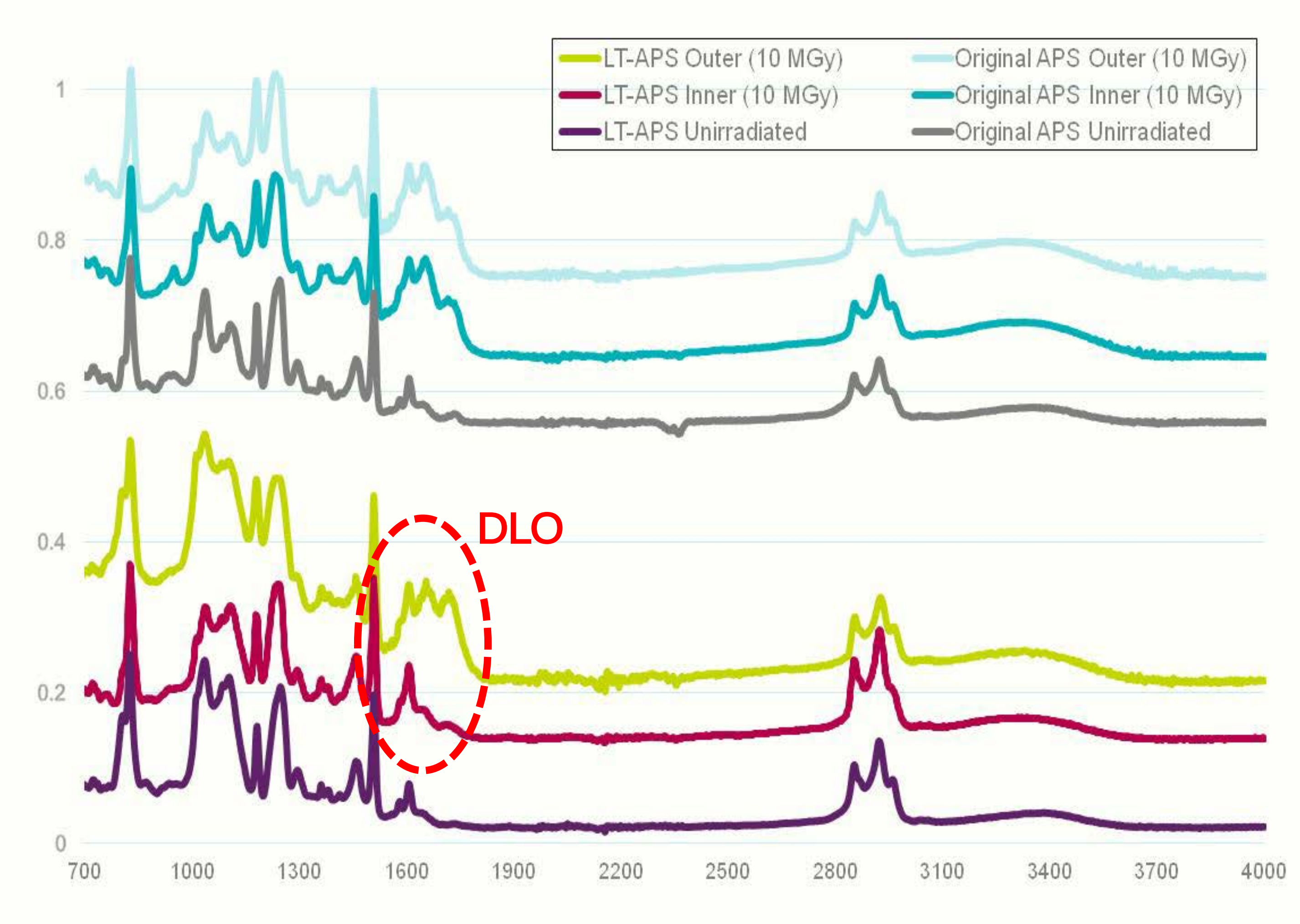
- Photographs of some of the candidate encapsulants before (top) and after irradiation to 10 MGy (bottom).
- From left to right: APS, Alchemix, Huntsman and VES.



# Results

- Compressive strength: Little change after irradiation to 10 MGy, however one formulation (Huntsman) softened to such an extent that it couldn't be measured.
- Flexural Strength: Significant reductions observed, particularly at lower dose rates.
- Gel Fraction measurements for each material were different e.g. the VES formulation cross linked in the initial stages of irradiation but at high doses oxidation chain scission dominated. The epoxies each showed steady decreases or increases in gel fraction.
- Gas Evolution: $G(H_2)$ values of ~ 0.6 or 0.8 were found for the epoxies. Conversely, VES generated little hydrogen ($G(H_2)$ 0.08) with the most prolific gases being CO and $CO_2$.

# Results - FTIR




- Epoxy formulations shown underwent oxidative chain scission after irradiation to 10 MGy:

  ~ 600 $cm^{-1}$ C=C bond formation
  ~1720 $cm^{-1}$ C=O formation
  ~ 3400 $cm^{-1}$ OH present

- Diffusion Limited Oxidation (DLO) Differences between the spectra taken from the surface and bulk

- DLO not observed for VES or other epoxy formulations.

# Results – Leach Tests

- TOC levels increased in the initial stages of irradiation, but decreased with increasing total dose.
- The decrease in TOC was attributed to radiolysis of the leached organic species.
- TOC levels in the thermally aged samples were higher.
- GC-MS data showed the most abundant organic species leached from the epoxy resins was benzyl alcohol whereas high levels of the cross-linking promoter, DMA, were found for VES.
- Ion chromatography showed high levels of chloride in the epoxies, which may be significant in terms of corrosion of metallic containers. Chlorides probably from the use of epichlorohydrin in precursor manufacture.

# Summary

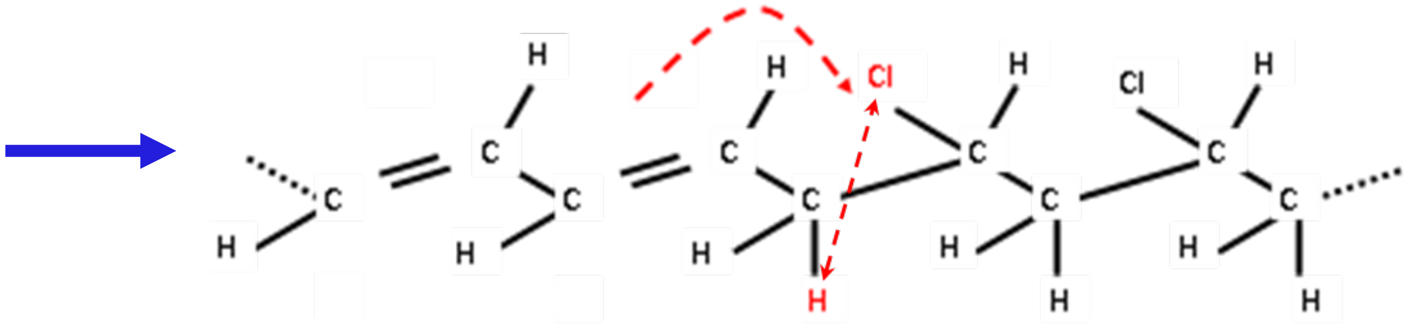
- Similiar formulations, even very closely related, show very different responses to the effects of radiation and thermal ageing.
- Compressive strength may not be an adequate indicator of ageing in these thermosetting polymers.
- The potential for unexpected chloride release in epoxy resins may affect the long-term performance of waste containers.
- NAPL and soluble organics were not found to be generated in high levels, providing reassurance in the chemical containment of the resins.

# Use of PVC in long-term waste storage

# Polyvinyl Chloride (PVC)

- PVC is used extensively throughout the nuclear industry in applications such as protective suits/tents and cables.
- PVC is a thermoplastic requiring an array of additives to protect it during processing and to impart other properties, e.g. inclusion of phthalates for flexibility.
- Whilst PVC has a wide range of useful properties, it will release HCl when it is exposed to radiation and/or heat.

Heat and/or radiation



# Case Study 2 – PVC Degradation

- Challenge
  - Our client wanted to better understand whether the rates of HCl release from PVC under different environmental conditions could cause corrosion issues during storage.

- Solution
  - Design an experimental programme to provide reliable HCl release data to underpin our development of a corrosion model.

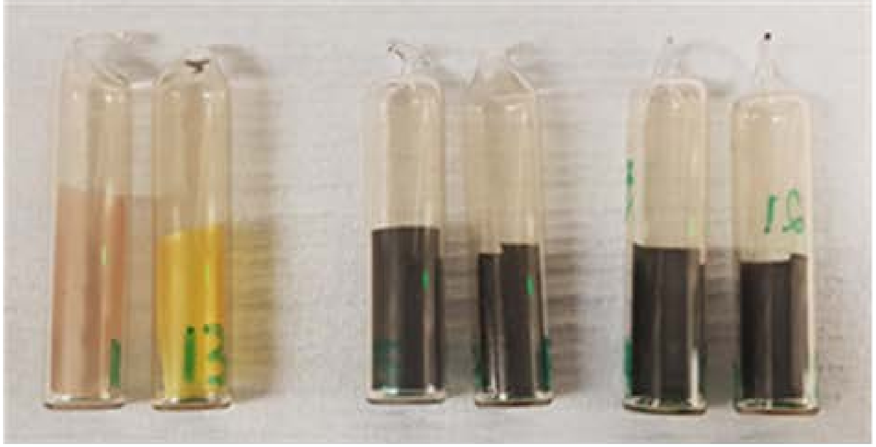
# Methodology (1)

- Devise a test methodology to reliably capture all HCl produced over a large matrix of ~500 samples.
- Adapted Jacobs gas analysis method:
  - Sample sealed in an inert glass ampoule
  - Gas release can be detected and accurately analysed. This approach has generated consistent radiolytic G-value data for a variety of polymers.
- Ageing Conditions:
  - 500 samples and 2 different PVC film materials
  - PVC samples encapsulated in glass ampoules under various environments;
    - Air
    - 95% humidity
    - Oxygen rich [40% $O_2$, 60% $N_2$]
    - Inert (Argon)

# Methodology (2)

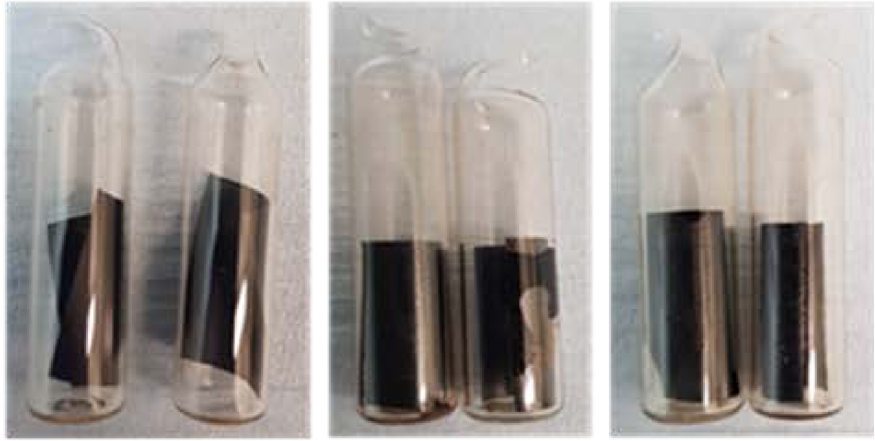
- Ageing Conditions:
  - Samples irradiated at an average dose rate of 0.58 Gy hr$^{-1}$ for 30, 180, 270 and 360 days
  - Combined radiation/thermal ageing at 80,100 and110° C
  - Additional samples exposed to thermal ageing only
  - Additional 'spot check' samples at 10 Gy hr$^{-1}$ to investigate the effect of different dose rates
  - Some ampoules intended for light gas analysis contained $NaHCO_3$ to neutralise the HCl
- PVC degradation and HCl release analysis:
  - pH and measurement of chloride in solution
  - Gas headspace analysis (Light gas and volatile organic compound (VOC))
  - Fourier transform infra-red spectroscopy (FTIR)

# Experimental Results – Visual Examination (1)



80°C 100 °C 110°C

180 Days - Air



80 °C 100 °C 110 °C

360 Days - Air

- Two types of PVC film – each pair of ampoules show PVC 1 on the left and PVC 2 on the right.
- Darkening and browning attributed to C=C formation but some additive degradation may also contribute to colour change.

# Experimental Results – Visual Examination (2)

- Appearance of phthalic anhydride crystals in some samples.
- Dendritic structures (shown in the red circles) – plasticiser degraded in oxygen.
- Acicular crystals - oxygen free environment (argon).

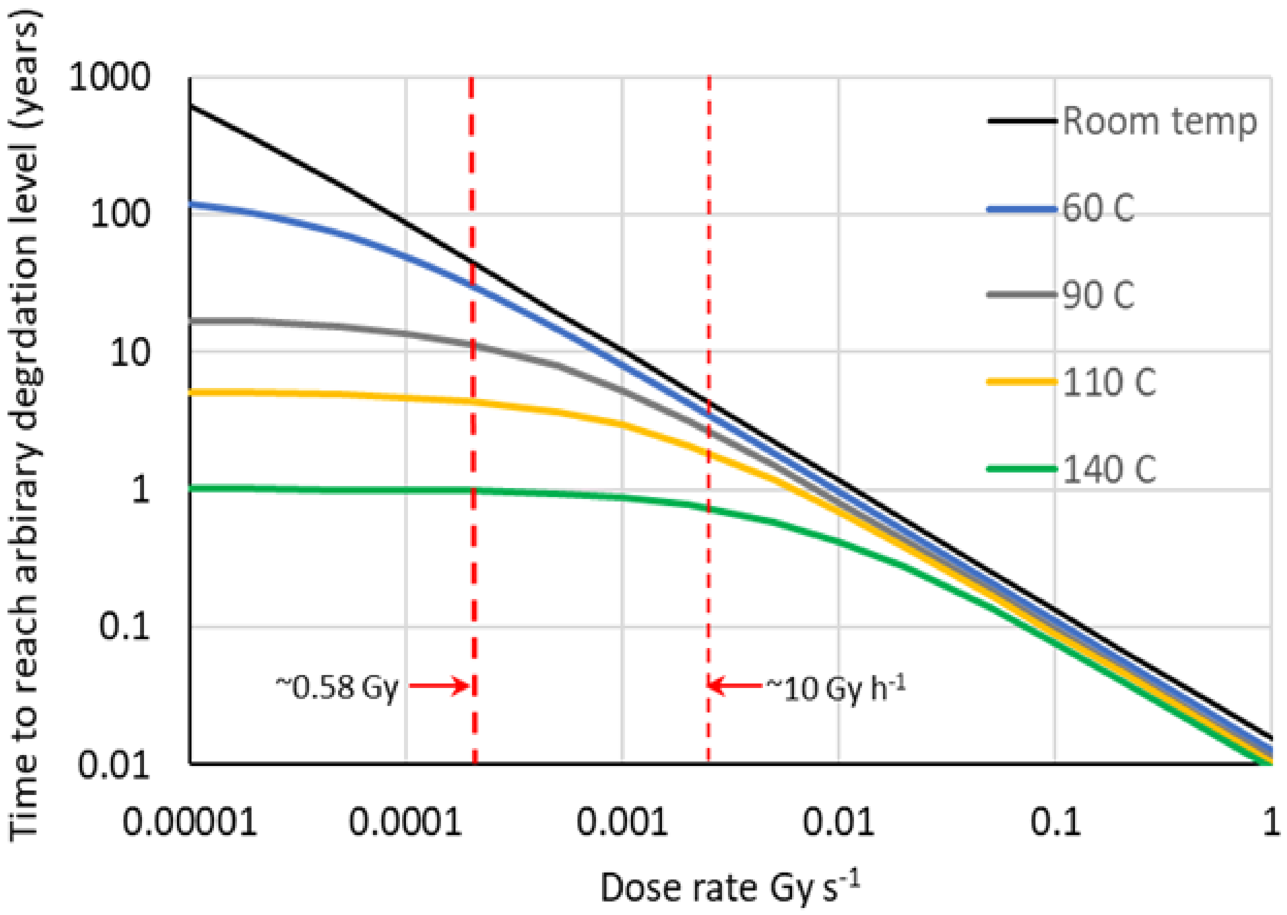
# Experimental Results – Radiolytic G-values

- Could HCl release rates be measured by G-values?
- Typical G-Values for HCl range between 0.1-10 molecules per eV
- Very high $G_{(HCl)}$ values were observed for both PVC materials!

| PVC type | Environment | Temperature (°C) | Ageing duration (days) | Radiation dose (kGy) | Number of Cl molecules released | $G_{(HCl)}$ molecules per 100 eV |
|---|---|---|---|---|---|---|
| PVC 1 | Air | 80 | 30 | 0.43 | 5.08E+17 | **122** |
| | | | 360 | 5.02 | 2.24E+19 | **461** |
| | | 110 | 30 | 0.43 | 3.13E+19 | **7476** |
| | | | 360 | 5.02 | 3.41E+20 | **7058** |
| PVC 2 | Air | 80 | 30 | 0.43 | 2.54E+17 | **63** |
| | | | 360 | 5.02 | 9.40E+19 | **196** |
| | | 110 | 30 | 0.43 | 1.73E+19 | **4157** |
| | | | 360 | 5.02 | 1.78E+20 | **3682** |
| PVC 1 | Argon | 80 | 30 | 0.43 | 2.54E+17 | **62** |
| | | | 360 | 5.02 | 8.13E+18 | **170** |
| | | 110 | 30 | 0.43 | 1.12E+19 | **2716** |
| | | | 360 | 5.02 | 3.63E+20 | **7537** |
| PVC 2 | Argon | 80 | 30 | 432.28 | 2.54E+17 | **61** |
| | | | 360 | 5020.48 | 1.04E+19 | **215** |
| | | 110 | 30 | 432.28 | 9.66E+18 | **2305** |

Definitely Not!

# Heat / radiation synergy effect




- Chart illustrating the thermal and radiation ageing characteristics of an arbitrary polymer Red dotted lines are the dose rates in this PVC ageing programme
- Influence of radiation stronger at 10 Gy $h^{-1}$.
- Heat may have little effect on degradation at high dose rates.
- Irradiation at a high dose rate at elevated temperature cannot accurately emulate synergies.

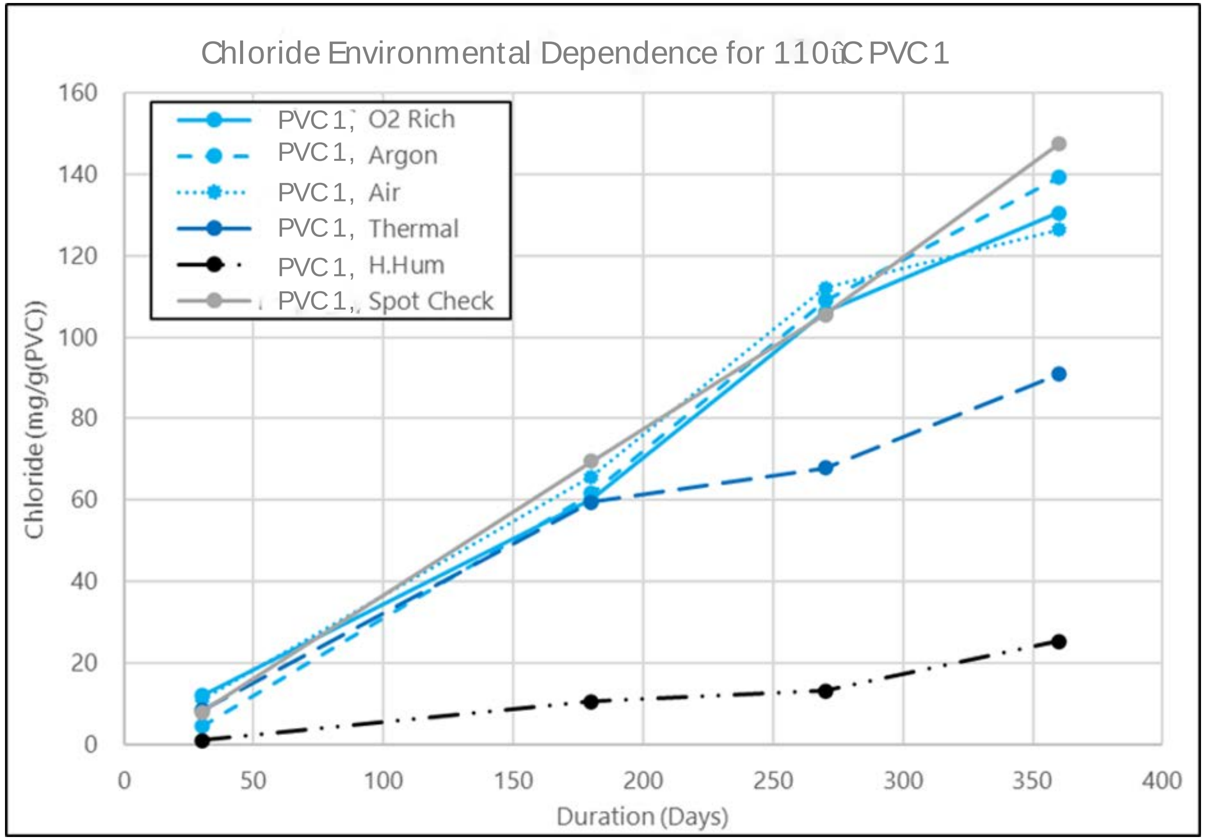
# Determination of chloride release rates

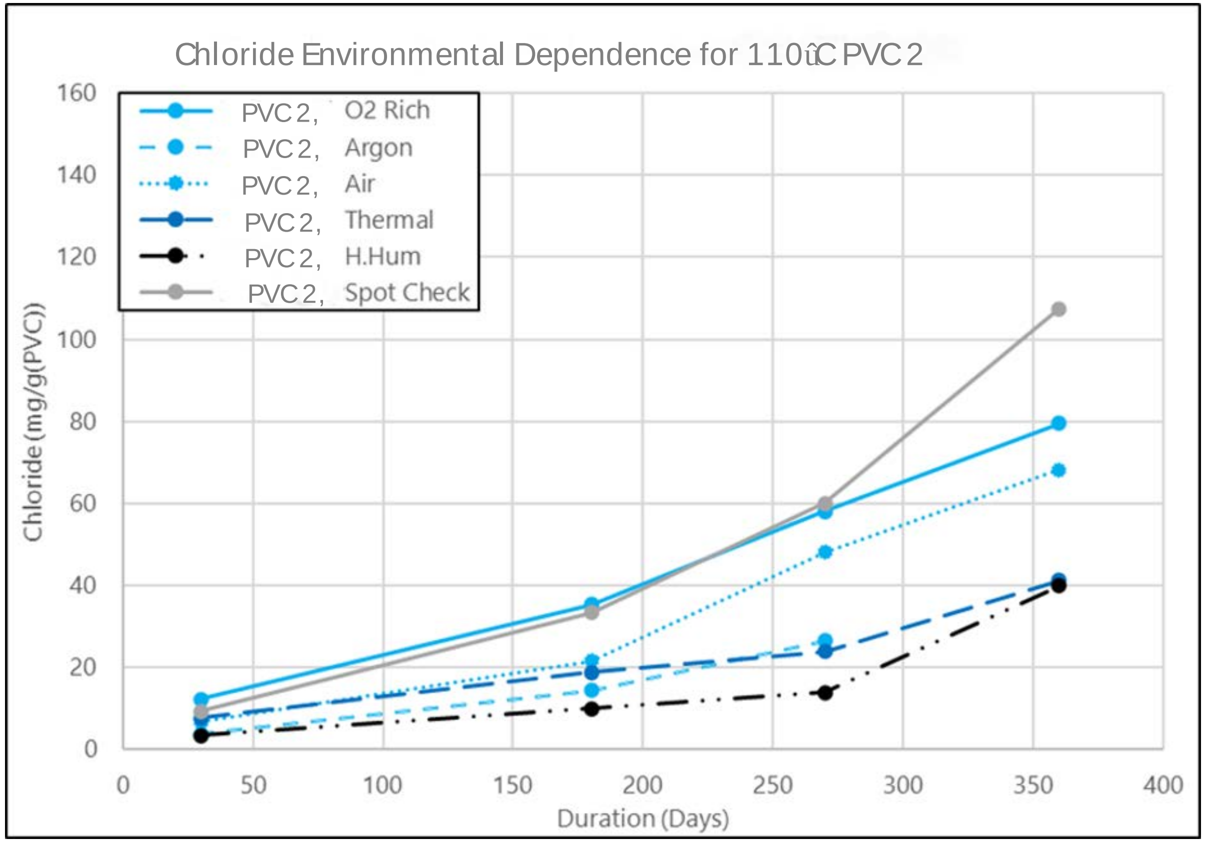
- The rate of release of HCl from the PVC films was shown to be temperature dependent at lower dose rates
- Our parameter of interest is therefore the activation energy ($E_A$) for HCl release
- Using the Arrhenius equation:

$$k = Ae^{\frac{-E_A}{RT}}$$

- Where:
  - $k$ is the rate constant for a given chemical process
  - $A$ is a coefficient of proportionality which is a constant for a given process and system
  - $E_A$ is an activation energy
  - $R$ is the ideal gas constant (8.31 J $mol^{-1}$ $K^{-1}$)
  - $T$ is the absolute temperature of the system

# Experimental Results – Cl$^-$ measurements



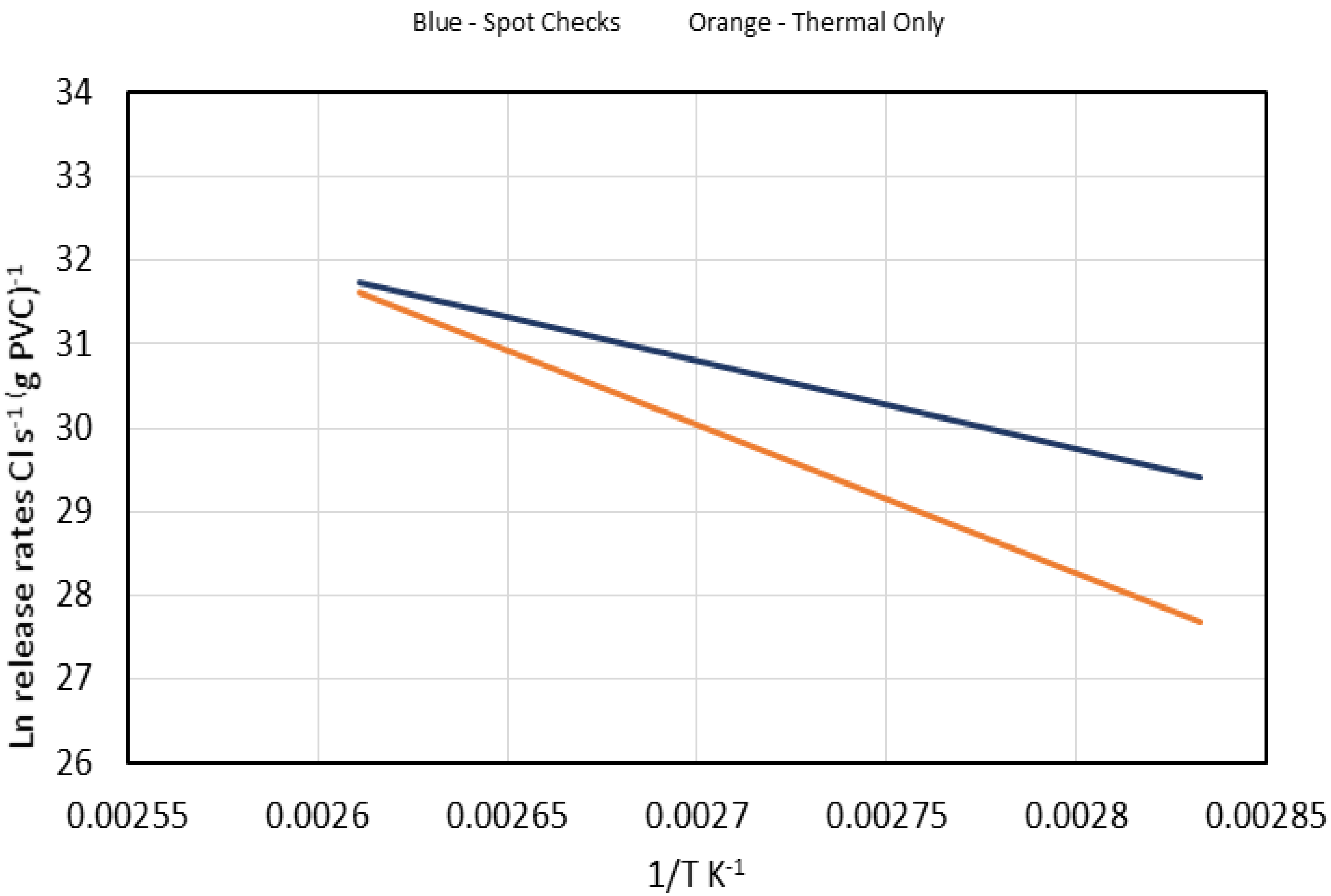



# Experimental Results – $E_A$ for the different environments

| PVC type | Environment | Average $E_A$ from the180, 270 and 360 days chloride release rates (kJ mol$^{-1}$) |
|---|---|---|
| PVC 1 | $O_2$ rich | 138 |
| | Argon | 164 |
| | Air | 128 |
| | High humidity | 111 |
| | Spot checks | 83 |
| | Thermal | 149 |
| PVC 2 | $O_2$ rich | 78 |
| | Argon | 76 |
| | Air | 110 |
| | High humidity | 81 |
| | Spot checks | 50 |
| | Thermal | 147 |

- Different PVC compositions – different response to radiation.
- Radiation/ thermal synergy effect.
- Similar $E_A$ values for both PVC types when thermal aged.
- Lower $E_A$ for irradiated samples especially spot checks at 10 Gy h$^{-1}$
- Unwise to completely rule out radiation if present or dose rate increases.

# Experimental Results – Activation energy for HCl release




- Increased dose rate, decreased $E_A$
- Increased dose rate, reduced temperature sensitivity.
- At high dose rate $E_A$ tends to zero. Thermal component will have little effect.
- The data suggests any significant increase in radiation dose rate will affect the accuracy of the $E_A$ approach.
- The test conditions are close to the threshold under which radiation effects may become significant.

## Summary

- A novel approach to ageing PVC under controlled heat and radiation was adopted from a gas analysis technique developed by Jacobs.
- This technique allowed all of the gaseous degradation products from the aged PVC to be captured for more accurate measurements.
- We were able to carry out analyses that improved our understanding of the degradation of plasticised PVC film.
- HCl release rates were determined and supported our development of a corrosion model for the determination of the long-term stability of metallic storage containers.
- We were able to establish that the dominant ageing process was thermal degradation under the ageing conditions.
- However, we determined that if dose rates increase much above 0.58 Gy $h^{-1}$, radiation effects and radiation/thermal synergy begin to dominate.

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# Thank you.

# Any Questions?

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## Important



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