

# National Technical Advisory Group – Elimination (NTAG-E)

Dr Norman Govan

Dstl Fellow

# NTAG – Elimination Research

- Team of SME's
- Tasked with identifying and assessing technical options that could be deployed in a range of operational scenarios
- Informs UK policy and planning



Cementation



Plasma Arc

# **Destruction of CW agents in Portland Cement**

Dr Stuart Notman  
Senior Scientist, Dstl

# Content

- Introduction and aims
- Experimental methods
- Results
- Conclusions so far...

# Introduction

- Cement based solidification/stabilisation is widely applied technique for immobilisation of inorganic waste
- Portland cement is an inexpensive and readily available resource worldwide
- Used in the production of **concrete**, a combination of cement and **aggregate** that sets and hardens to form a strong building material
- Tri- and di-calcium silicates ( $C_3S$  and  $C_2S$ ) comprise over 80% by weight of most Portland cements

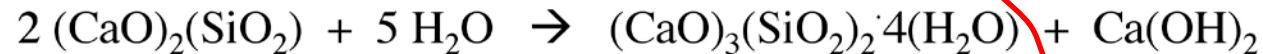
● $C_3S$	Tricalcium Silicate
● $C_2S$	Dicalcium Silicate
● $C_3A$	Tricalcium Aluminate
● $C_4AF$	Tetracalcium Aluminoferrite
● $CSH_2$	Gypsum

# Fate of chemical agents absorbed in hardened concrete

- The highly alkaline environment found in hardened concrete is known to accelerate the degradation of CW agents
  - Reports indicate that, VX only persists for days. These studies also indicate that VX degradation was selective for EMPA, no VX-acid was detected by  $^{31}\text{P}$  NMR
  - Half-lives for HD on hardened concrete range from 3.5 to 54 weeks. Half-life dramatically reduced when the substrates were moistened
  - Half-lives for GB vapour on cement paste is in range of 20 minutes to 5 hours. Half-life reduced further as humidity increases
- No data on agents in hydrating cement

# Cement hydration

- Cement hardens by hydration - a chemical reaction between the anhydrous **cement** powder and **water**.
- Reaction conditions in the slurry (paste) closely mirror those found in chemically aggressive CBW decontaminants.
- Initial hydration (that persists for minutes to hours) is marked by rapid heat evolution and the release of hydroxyl ions into solution, producing a pH near 13.



- Extent that CW agents may inhibit setting (hydration process) is unknown

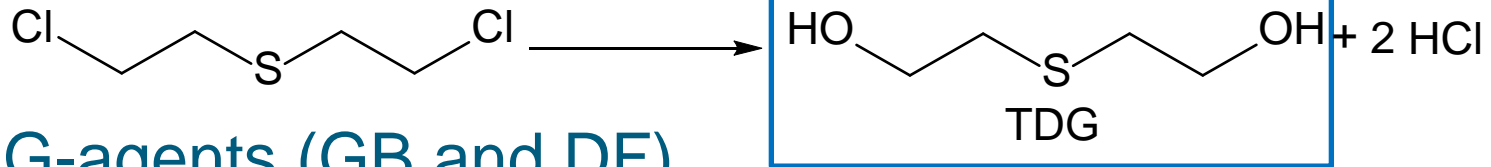
# Aim

- To determine whether the physico-chemical properties of Portland cement can be used to destroy practical quantities of CW agents.

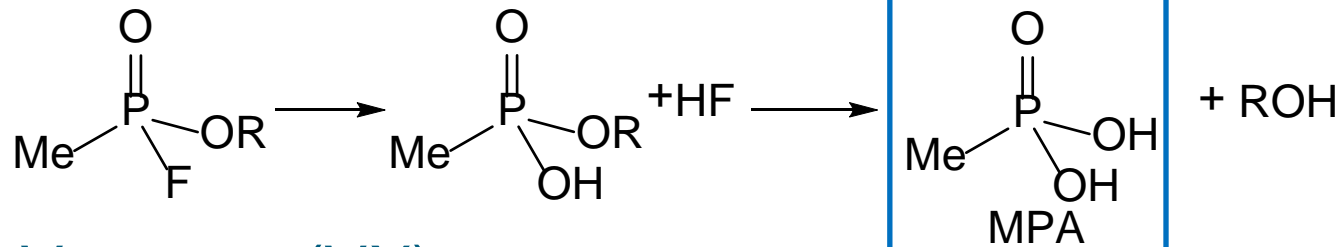


# Agents

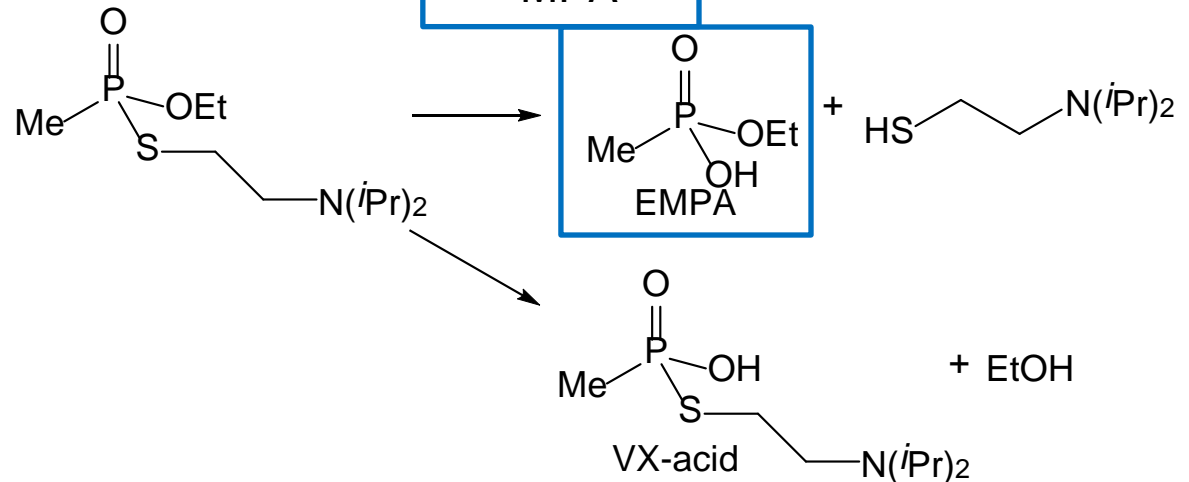
- Sulfur mustard (HD)



- G-agents (GB and DF)

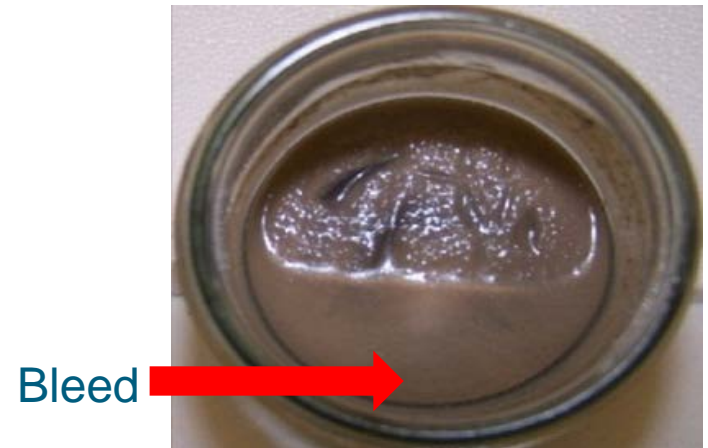


- V-agents (VX)



# Experimental Method

- Aqueous solutions of reaction products (at 1, 5, 10, 25 and 50 %w/w) mixed with cement powder at 0.5 and 0.8 liquid to cement (l/c) ratio's (0.3 to 24 %w/w of the total weight)
- Setting time compared to control cement paste
- Bleed liquid that formed on the surface of the cement pastes during setting was sampled to monitor reactivity
- Extent to which encapsulated chemicals could be leached from hardened cement paste assessed at 28 days.



# Method development

Rapid mixing of EMPA and MPA at high concentrations

Vigorous reaction

Minimal/no bleed liquid

Formed gravel

Requires controlled addition and neutralisation



Control

8.3 %w/w MPA



# Controlled Addition

- Capacity of cement for MPA increased by a factor of 2 (8.9 %w/w of total) when
  - Pre-add 10 %w/w calcium hydroxide to cement paste
  - Addition over 1 hour
  - Extended stirring time (3 hours)



# Reaction of GB and DF

- Complete neutralisation of GB and DF in 24 hrs
- No GB or DF was detected in bleed water,
- Only trace quantities of reaction products IMPA/MPA in bleed
- Increases the set times
  - 2.2 %w/w GB – 2 day
  - 8.9 %w/w GB (0.8 ratio) – 3 weeks
  - 9.0 %w/w GB (0.5 ratio) – did not set
  - 2.2 %w/w DF – 7 days

GB

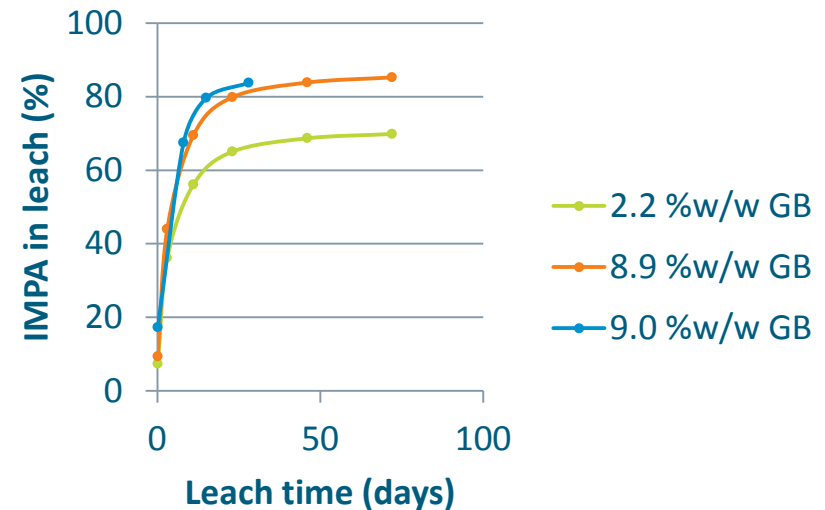
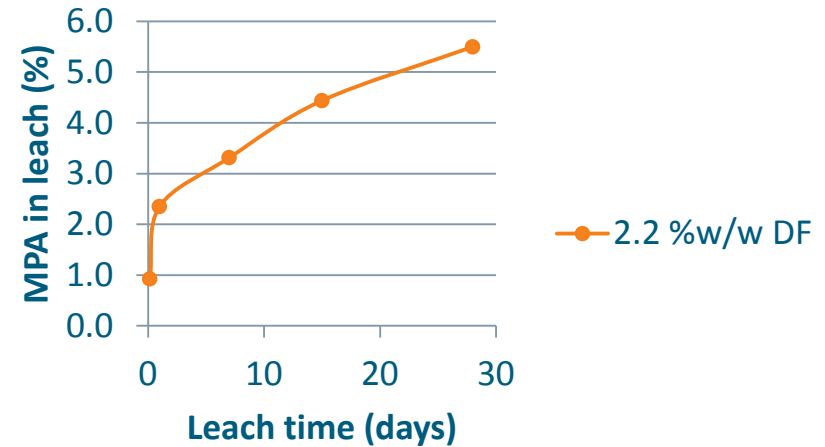


DF



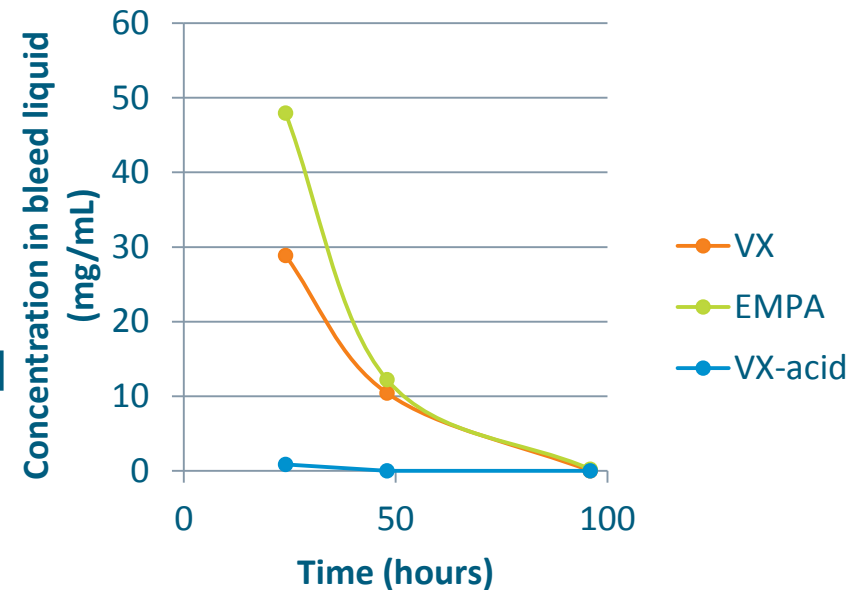
# Leaching from cement (GB,DF)

- No GB or DF was detected in leach
- Low levels of MPA detected in DF leach
- Substantial quantities of IMPA
- Requires inclusion of bespoke additive



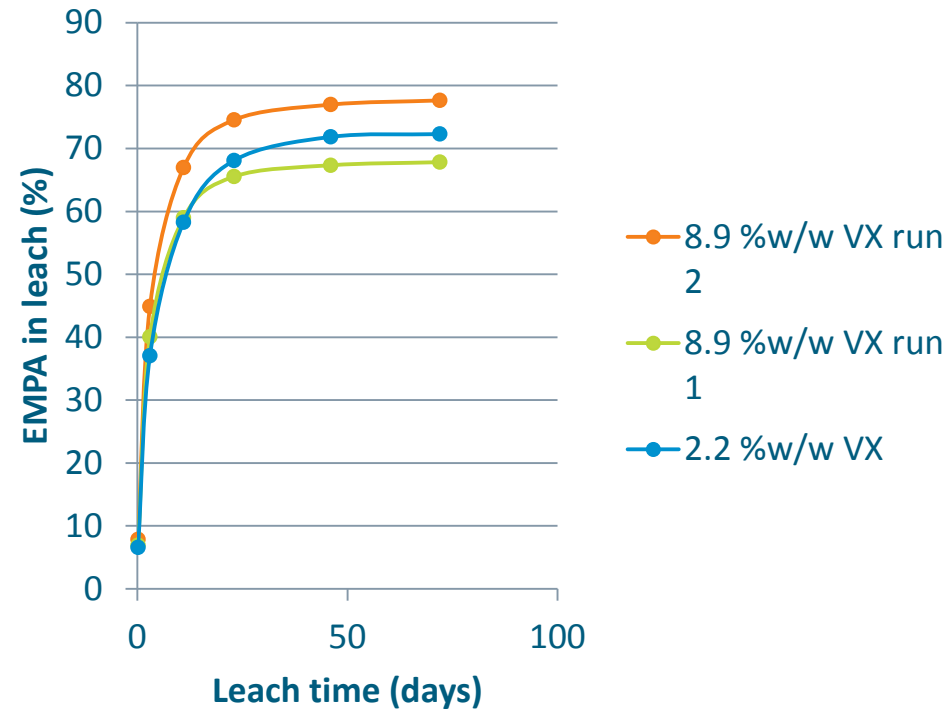
# VX reaction in cement

- Complete destruction of VX in 4 days
  - But takes 2 weeks to set
- Oil on surface of paste, identified as di-sulfide
- At high VX loading 8.9 %w/w
  - Low levels of toxic VX-acid detected in bleed
  - Complete uptake of bleed liquid at 96 hours



# Results from leach studies - VX

- No VX or VX-acid detected in leach
- However, significant quantity of EMPA recovered from leach samples
- Requires inclusion of bespoke additive





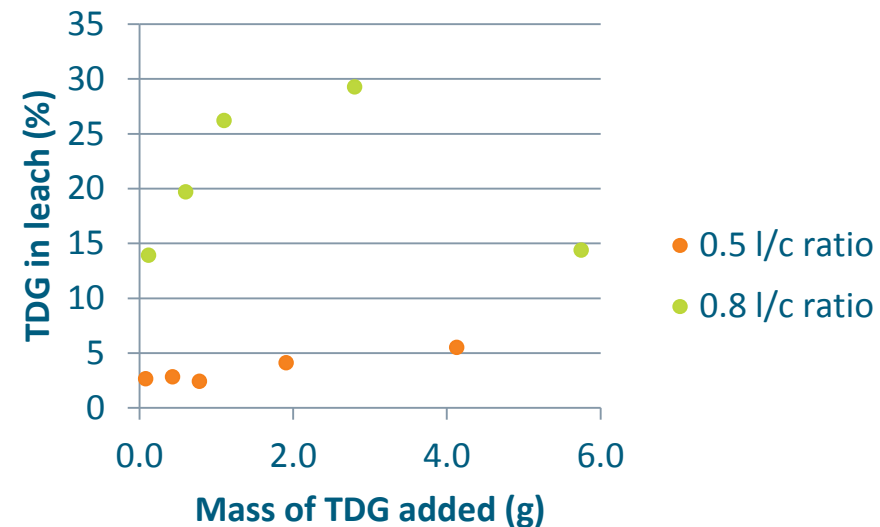
# Thiodiglycol (TDG)

- High capacity for TDG in cement
  - Slowed initial setting time by 5 days and appearance slightly different (50 %w/w TDG solution)
  - Significant quantity of TDG in bleed
- Significant quantities of TDG recovered from leach
  - 0.8 l/c ratio pastes more porous

Control

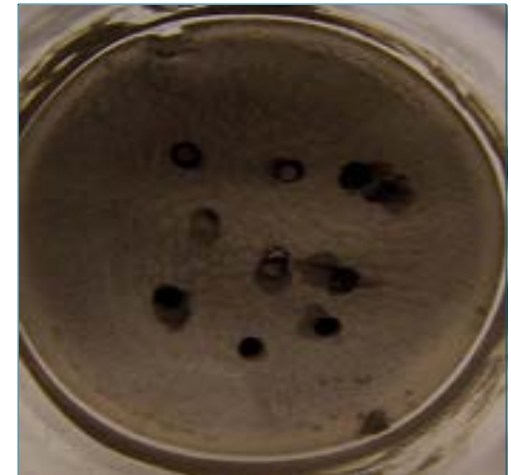


50 %w/w TDG solution



# Reaction of mustard in cement -

- Incomplete neutralisation of HD
  - 62 % of HD added removed from surface after 24 hours
- Methanol was added to the cement paste to dissolve HD
  - This prevented the cement setting
  - Reduces amount of HD in bleed to 24 %
- Low levels of HD detected in chloroform extract of leach



# In summary

- Mixing CW agent into hydrating Portland cement offers the potential to destroy large quantities GB and VX
  - Estimate that for GB and VX, 5 kg of agent could be neutralised using a 25 kg bag of cement and 15 kg of water
- Further work required to prevent hydrolysis products leaching from the cement
- The current system is not effective for destruction of HD
- Ongoing programme seeks to develop specialist cement able to prevent leaching of reaction products and develop a practical system for HD

# Acknowledgements

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