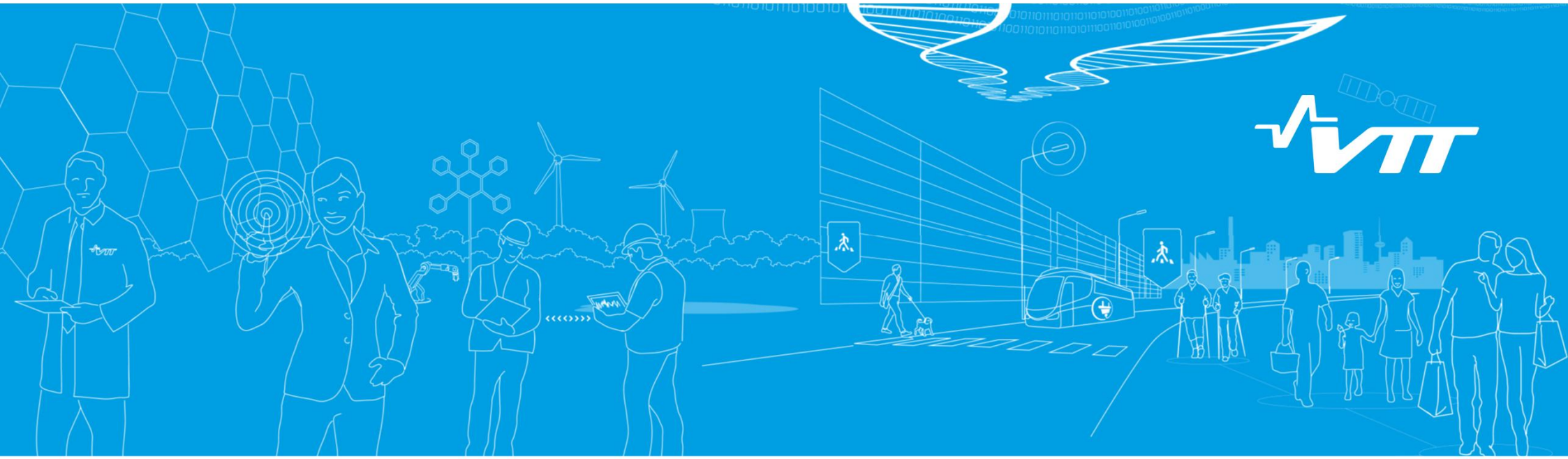

# Bentonite-water-copper interaction studies during 15 years

BOA seminar

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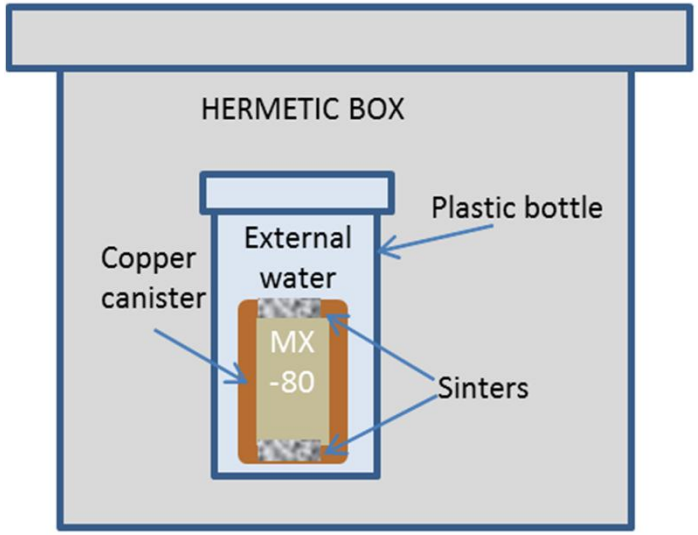
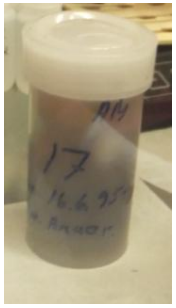
# Experimental arrangements

- 2 experiments, aerobic and anaerobic conditions
- Pre-saturated MX-80 (30g), 1.5 g/cm$^3$
- Water (Allard): fresh water (100ml).
- Copper (surface 90 cm$^2$)
- Time: 0, 10 months & 15 years
- Analyses and measurements: microstructure (Michal), chemistry (Joonas), mineralogy (Mia), bacteria activity (Pauliina) and modelling (Aku).



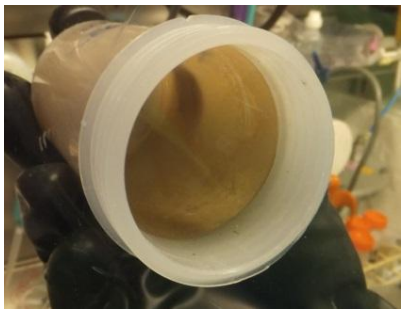

Aerobic



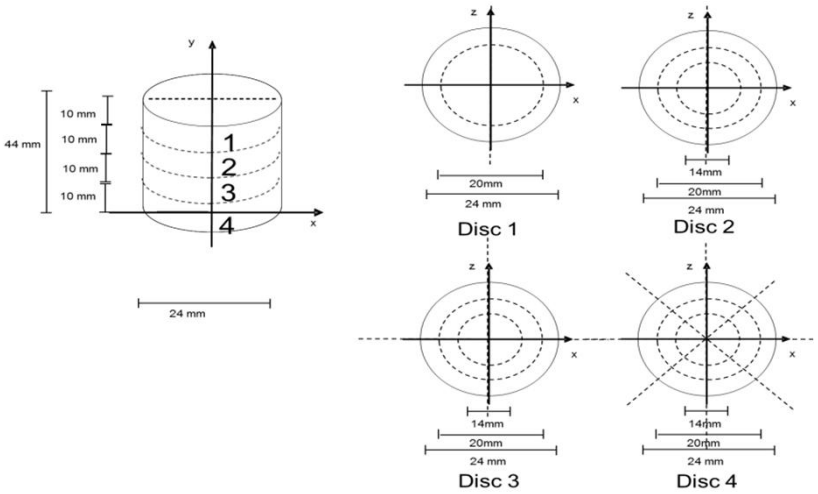


Anaerobic





# Post-mortem analyses and measurements



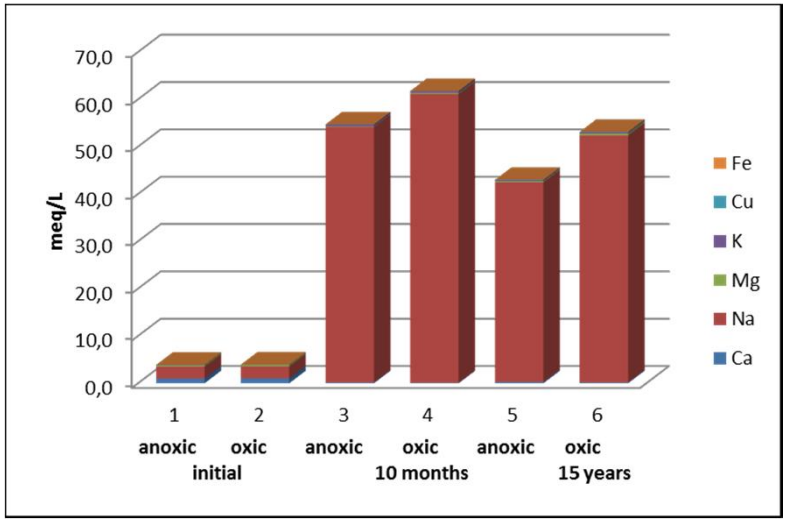

| Analysed property | Method |
|---|---|
| **Water analyses** | |
| $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$,$Cu^{2+}$, HSiO3, Fe(II), Fe(tot) | ICP-OES |
| $Cl^-$ & $SO_4^{2-}$ | IC |
| Alkalinity ($HCO_3^{2-}$) | Titration |
| pH, $S^{2-}$ | Electrode |
| **Plastic bottle** | |
| $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$,$Cu^{2+}$, | Stripping + ICP-OES |
| | |
| **Bentonite analyses and measurements** | |
| Water content | Weight loss at $105^0$C |
| Total carbon and sulphur | ELTRA |
| Organic carbon | Acid dissolution + ELTRA |
| Aqueous Leachates | Dissolution in deionized water |
| CEC | Cu-Trien method |
| Exchangeable cations | Exchange with $NH^{4+}$ in ethanol |
| Accessory minerals | SEM+INCA and EPMA |
| Microstructure | SAXS+NMR |

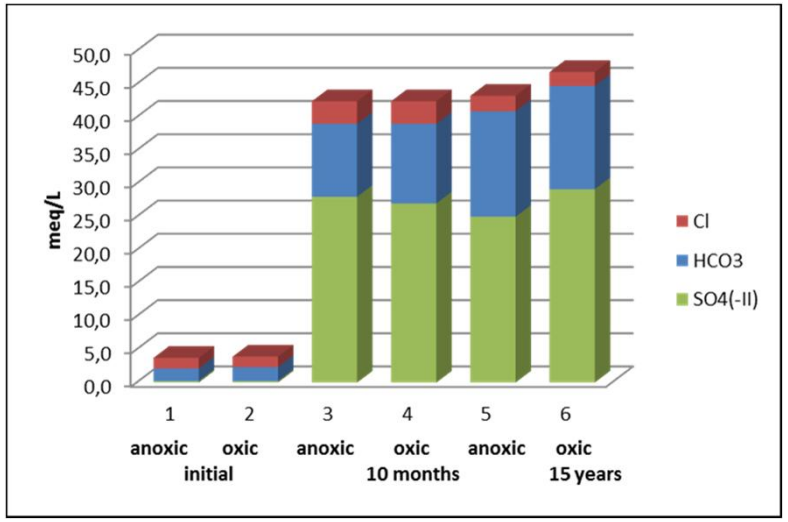
# Water analyses

| | Initial conditions | | after 10 months | | after 15 years | |
|---|---|---|---|---|---|---|
| | anaerobic [meq/L] | aerobic [meq/L] | anaerobic [meq/L] | aerobic [meq/L] | anaerobic [meq/L] | aerobic [meq/L] |
| pH | 9,2 | 8,4 | 8,5 | 9,5 | 9,1 | 9,5 |
| Cations | **3,9** | **4,0** | **54,7** | **61,8** | **43,0** | **53,2** |
| Ca | 1,0 | 1,1 | 0,2 | 0,1 | 0,3 | 0,2 |
| Na | 2,5 | 2,5 | 54,0 | 61,0 | 42,2 | 52,2 |
| Mg | 0,3 | 0,3 | 0,1 | 0,2 | 0,2 | 0,4 |
| K | 0,1 | 0,1 | 0,4 | 0,5 | 0,3 | 0,3 |
| Cu | 7,6E-05 | 0,0E+00 | 4,0E-03 | 0,0E+00 | 6,0E-03 | 2,6E-02 |
| Fe | 0,0 | 0,0 | 0,0 | 0,0 | 1,8E-03 | 5,7E-04 |
| Fe(II) | max. 2,7 | | NA | NA | | |
| Anions | **3,7** | **3,9** | **42,4** | **42,4** | **43,2** | **50,0** |
| HCO3 | 1,9 | 2,1 | 11,0 | 12,0 | 15,9 | 15,6 |
| CO3 | | | | | | 3,2 |
| Cl | 1,6 | 1,6 | 3,4 | 3,4 | 2,3 | 2,1 |
| SO4(-II) | 0,2 | 0,2 | 28,0 | 27,0 | 25,0 | 29,1 |
| S(-II) | - | - | - | - | <0.3µM | <0.3µM |

Dissolution of CaCO3

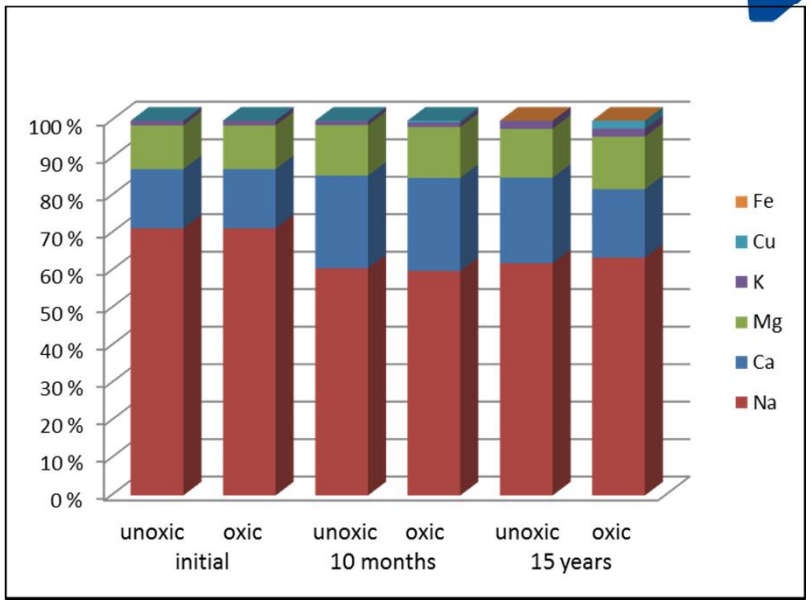
Dissolution of CaSO4



# Bentonite analyses

- CEC ”decrease” => $CaSO_4$
- EC: Mono → divalent
- EC: Presence of Cu & Fe after 15 y
- Accessory minerals
  - CO3: calcite, siderite, malachite
  - SO4: barite
  - S: pyrite, Cu-Fe-S
  - org_C: ?

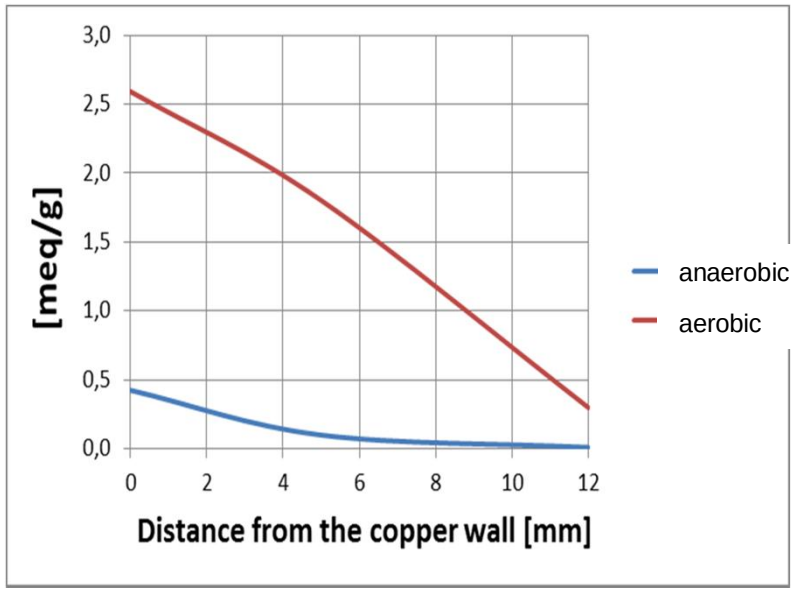


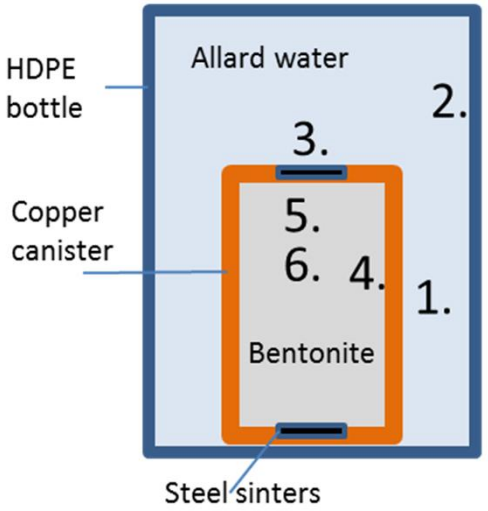

| | Initial conditions | | after 10 months | | after 15 years | |
|---|---|---|---|---|---|---|
| | unoxic | Oxic | unoxic | Oxic | unoxic | Oxic |
| dry density | 1,5 | 1,5 | 1,5 | 1,5 | 1,5 | 1,5 |
| **Montmorillonite** | | | | | | |
| **Exchangeable cations** | [meq/100g] | [meq/100g] | [meq/100g] | [meq/100g] | [meq/100g] | [meq/100g] |
| Ca, (meq/100g) | 15 | 15 | 23 | 23 | 21 | 17 |
| Na | 66 | 66 | 56 | 55 | 57 | 59 |
| Mg | 11 | 11 | 12 | 13 | 12 | 13 |
| K | 1 | 1 | 1 | 1 | 2 | 2 |
| Cu | 0 | 0 | 0,05 | 0,485 | 0 | 2 |
| Fe | | | | | 0 | 0 |
| **CEC [meq/100g]** | 104 | 104 | 98 | 97 | 92,41 | 92,48 |
| **Accessory minerals** | **[mg/$g_{clay}$]** | **[mg/$g_{clay}$]** | **[mg/$g_{clay}$]** | **[mg/$g_{clay}$]** | **[mg/$g_{clay}$]** | **[mg/$g_{clay}$]** |
| CO3 | NA | NA | NA | NA | 3,65 | 2,91 |
| SO4 | NA | NA | NA | NA | 0,48 | 0,45 |
| S | NA | NA | NA | NA | 0,99 | 1,03 |
| org C | NA | NA | NA | NA | 1,95 | 1,86 |

# Copper analyses

- Amount of the copper as exchangeable cations decrease as function of the distance from Cu wall

- Copper was found under oxic conditions
  - Exchangeable cations
  - Accessory minerals (oxic)
  - External water
  - Plastic bottle surface



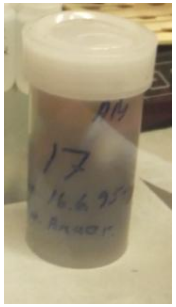

REACTIONS

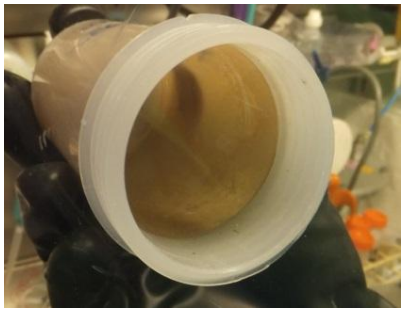
1. copper-water
2. Copper-HDPE bottle
3. Copper-sinter (steel)
4. Copper(s)-bentonite (surface)
5. Copper(I)-bentonite
6. Copper(I)-montmorillonite

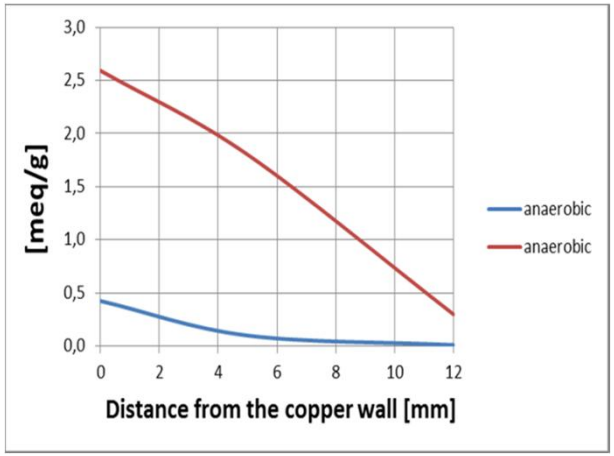
# Conclusion

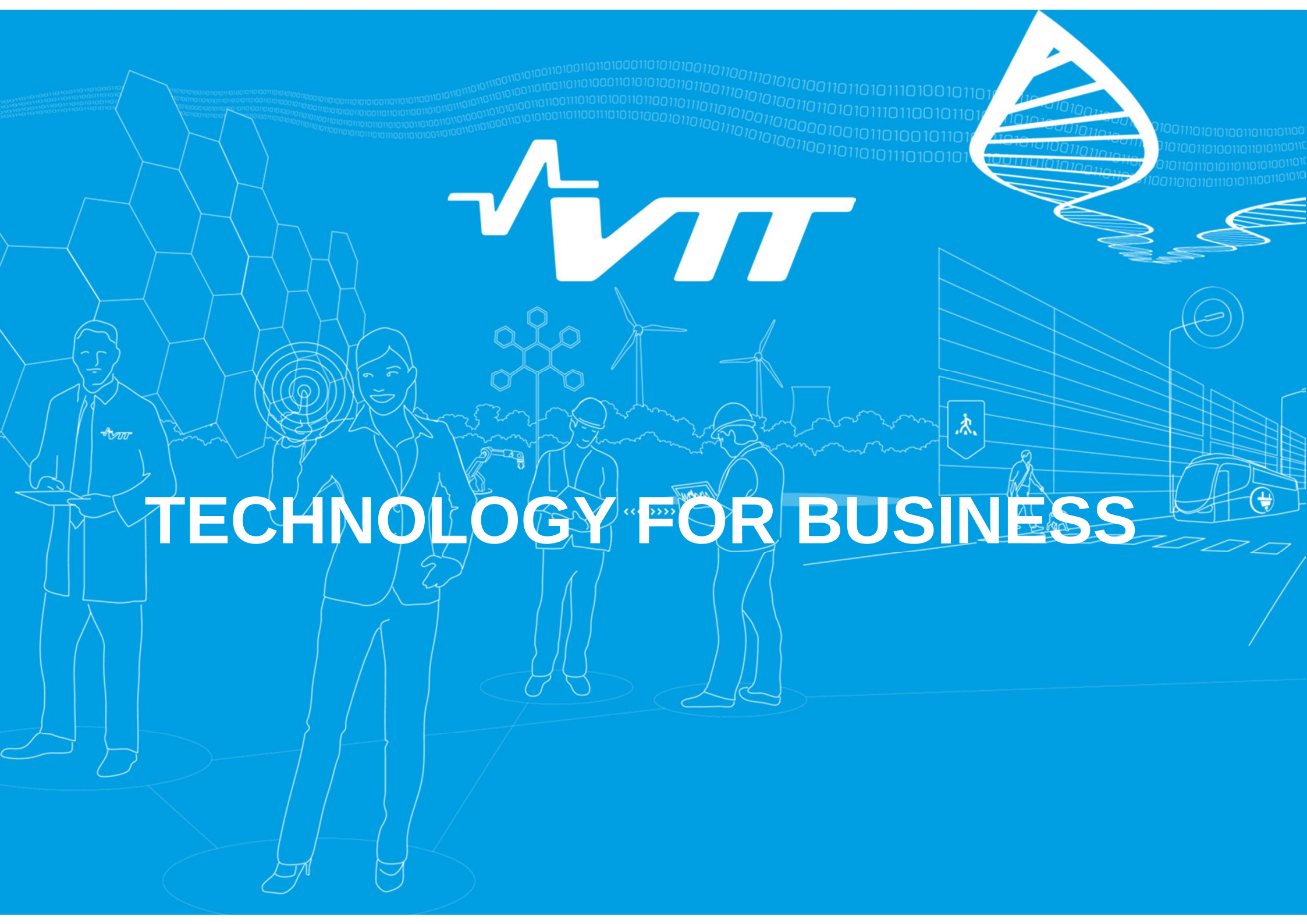
- The main chemical processes, like dissolution of gypsum and calcite, exclusion of anion products from bentonite and exchange of cations (calcium with sodium) were observed to occur during 10 months interaction. No significant changes have been observed in these processes between 10 months and 15 years experiments.

- copper diffusion in bentonite, precipitation as cuprite and malachite in bentonite, and replacing partly other cations as exchangeable cations in the experimental under aerobic conditions. The amount of the carbonates increased in external water, and calcite and siderite were observed in bentonite after 15 years. Part of the dissolved copper were found from the surface of the plastic canister.





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