CHEMICAL OXIDATION – FROM LABORATORY INVESTIGATION TO FULL SCALE REMEDIATION

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Presentation focus:

- Problem formulation - PCB contamination in the Czech Republic
- PCB treatment possibilities
- Laboratory scale testing
- Pilot scale verification
- Application methodology for full scale
- Conclusions

PCB – basic information:

- Mixture differing by chlorination stage and positions (1 to 10 Cl on biphenyl)
- Use since 1920's due to their properties
- 209 congeners, 102 of them broadly used
  - Aroclor (USA, UK), Clophen (Germany), Delor (former Czechoslovakia), Kanechlor (Japan)
- Since 1970 to 1980's PCB production was gradually closed down
- Consequence => persistence in the environment and in fatty tissues, accumulation in food chains

PCB in the Czech Republic:

- Low concentrations – large volume of soil containing residual percentages of PCB
- Asphalt mixing plants – e.g. Milevsko, Holostredy, Mecholupy, Horsovsky tyn
  - since 1950's, approx. 70 in operation
  - heating media spillages (Delor 103 and 106)
- Machine-works – e.g. Policka, Blansko, Brno, Tisnov, Sezimovo usti
  - hydraulic and transformer oil spillages
- Distribution electric stations (less common)

Asphalt mixing plant in Milevsko:

PCB – treatment possibilities:

- Thermal – special combustion equipment, air emission treatment system, expensive, heavily contaminated materials
- Biological – bacterial strains capable to utilize some congeners, cheap, long-term, low contamination
- Chemical – powerful agents (Fenton, ozone, persulphate), reasonable costs, short-term, dangerous chemicals
- Others – flushing with surfactants – under R&D, reasonable costs, medium-term, contamination movement to another phase

PCB – chemical oxidation:

- Powerful oxidizing => cleavage of PCB rings and elimination of chlorine ions
- Degradation mechanism does not depend on congener type (non-selective reaction)
- Applicability of Fenton reagent and ozone already confirmed
- Combination chemical / biological treatment - chemical pre-treatment increases PCB biodegradability 7 times

Laboratory scale testing (1):

- Contamination characterisation:
  - PCB = Delor 103 and 106
  - individual congeners = 28,52,101,138,153,180
  - other = TPH, residues => TOC
- Soil properties:
  - organic carbon = TOC
  - inorganic compounds = metals, carbonates
  - pH, specific conductivity, redox potential (DO, CO_2)
  - grain size = sieve analysis
  - (others - porosity, permeability)

Laboratory scale testing (2):

- Laboratory testing in 2003 and 2004:

– Milovice – up to 100 mg Σ PCB.kg^{-1} (cong. 28 = 60%, cong. 52 = 25%), TPH, TOC 9.5 g.kg^{-1}

  – other parameters: size > 0.250 mm 60%, pH 6.6, conductivity 7.58 mS.cm^{-1}, ORP -19

– Milevsko – up to 200 mg Σ PCB.kg^{-1} (cong. 28 = 78%, cong. 52 = 18%), TOC 8.4 g.kg^{-1}

  – other parameters: size < 0.063 mm 45%, pH 7.3, conductivity 7.55 mS.cm^{-1}, ORP -23

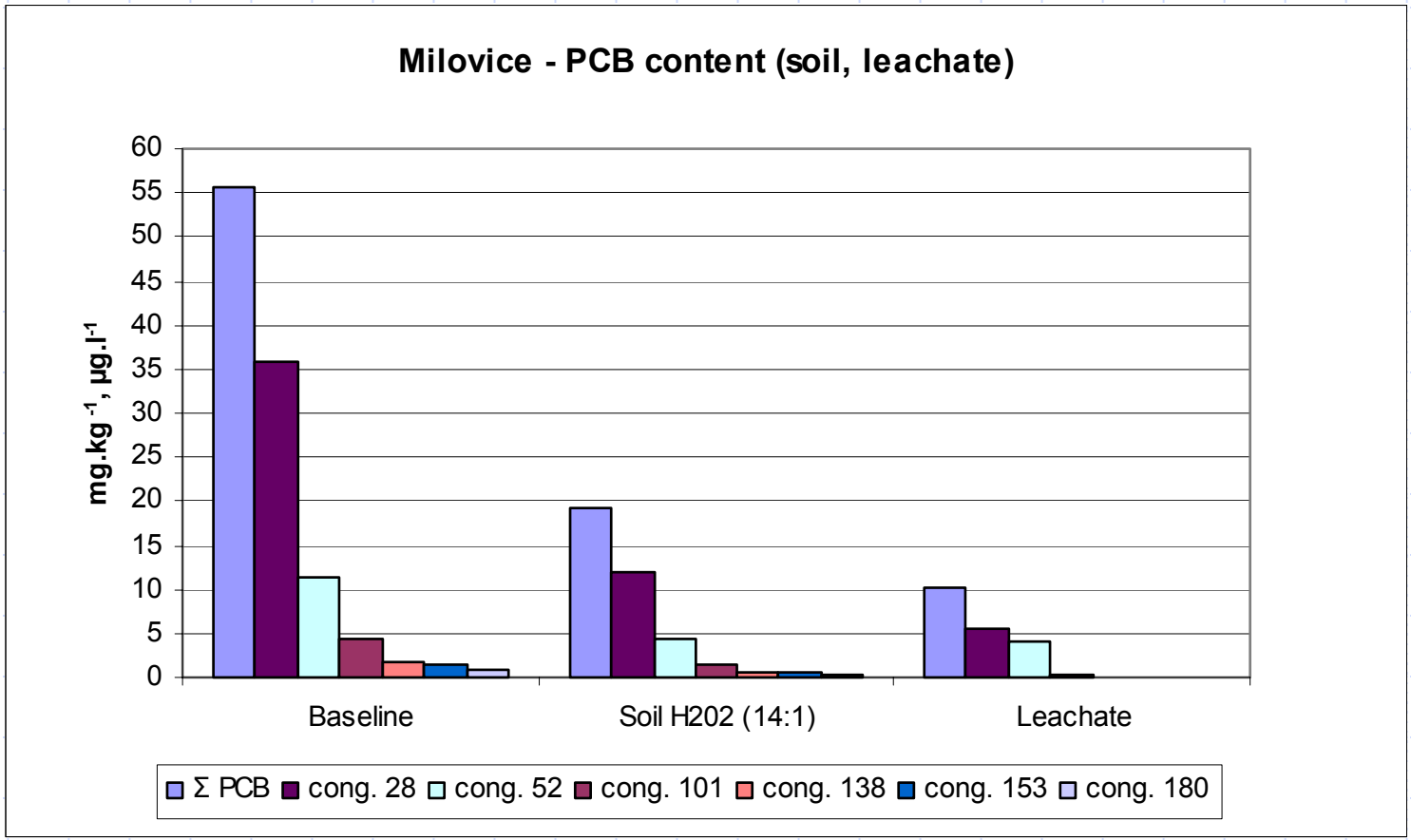
Laboratory scale testing (3):

- Testing on 200 g samples with 100 ml water
- Various combination of $FeSO_4$ and 17.5% hydrogen peroxide with acid addition
- Oxidant/TOC Ratios 4:1 – 14:1
- Tested batch and semi-continuous applications
- Observed parameters:
  - pH, temperature, conductivity, ORP, others
  - PCB content, TOC – soil, leachate
  - ecotoxicology tests (luminescence bacteria, Daphnia magna)
  - dioxine emission

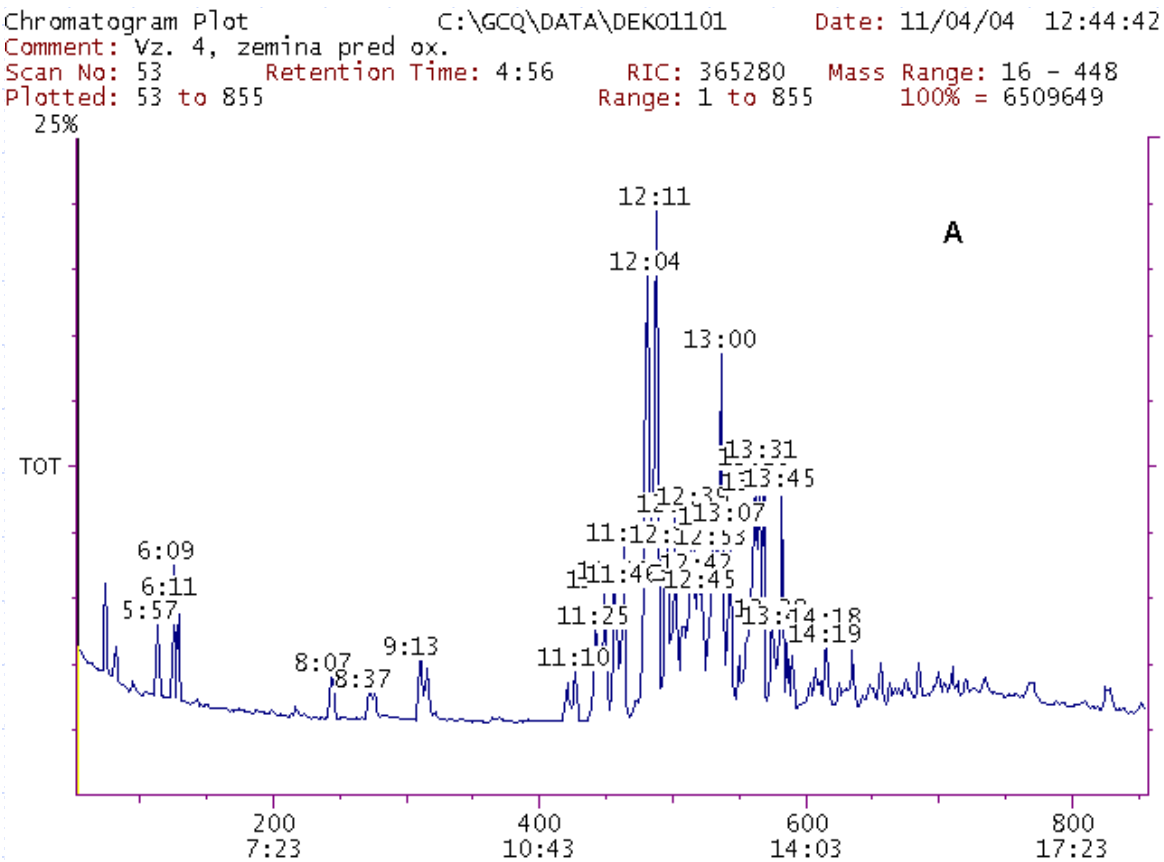
Laboratory scale testing (4):

- All variants showed:
  - PCB removal up to 90% (14:1 ratio)
  - PCB content in leachate < 10 $\mu g.l^{-1}$
- Process parameters: pH increasing up to 6, ORP decrease (from 90mV), temperature peak around 70°C
- Ecotoxicity drop in all reacted samples
- Not observed selective congener oxidation
- Not observed effect of semi-continuous oxidant application
- Not observed creation of PCDD/PCDF
- Not detected low molecular oxidation products

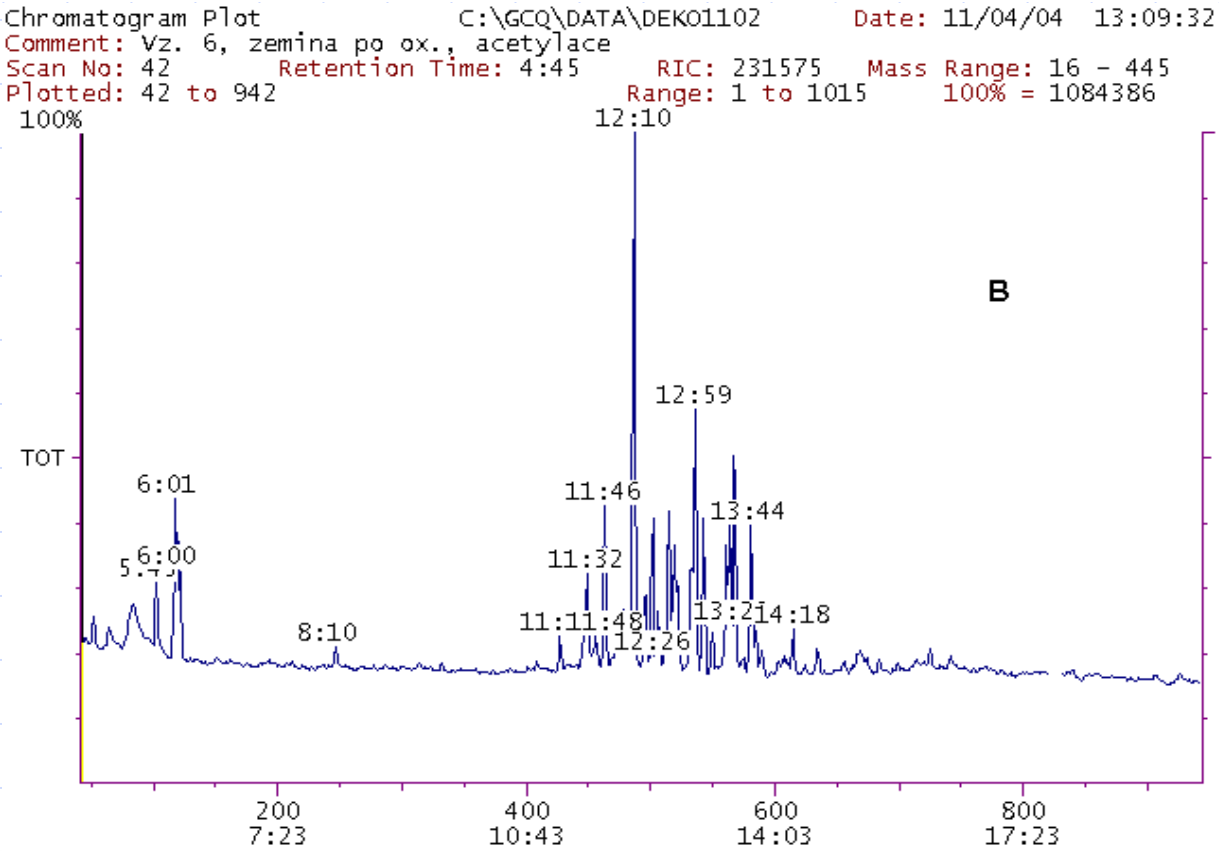
PCB content:



GC/MS analysis – before oxidation:



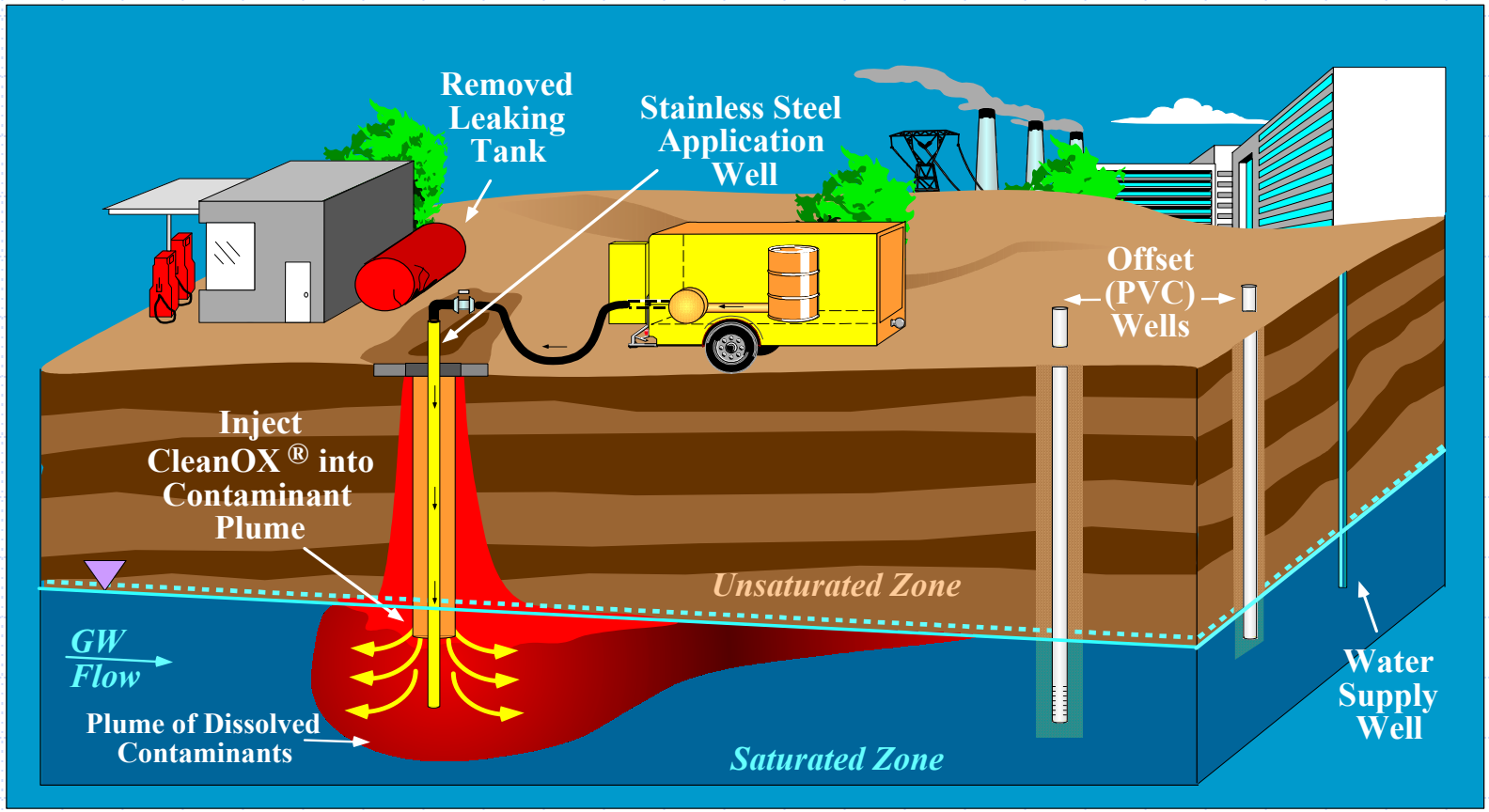
GC/MS analysis – after oxidation:



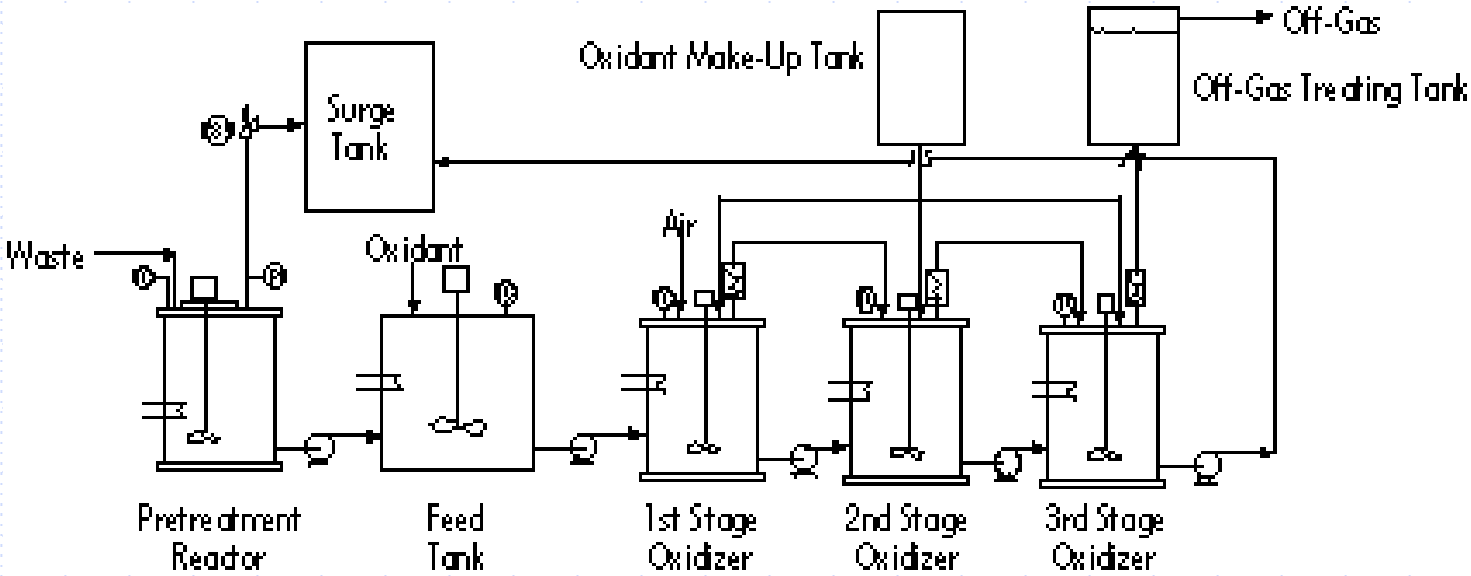
Pilot scale verification (1):

- Depends on application (in-situ vs. ex-situ)
- Verification of chemical mass for treatment and its efficiency predicted from laboratory experiments
- Determination of time for applying chemical mass
- Infiltration rate (low pressure, temperature)
- Radius of influence
- Parameters: temperature, OPR, conductivity, pH (DO, CO_2, steam)
- Others – off-gas monitoring (ex-situ)

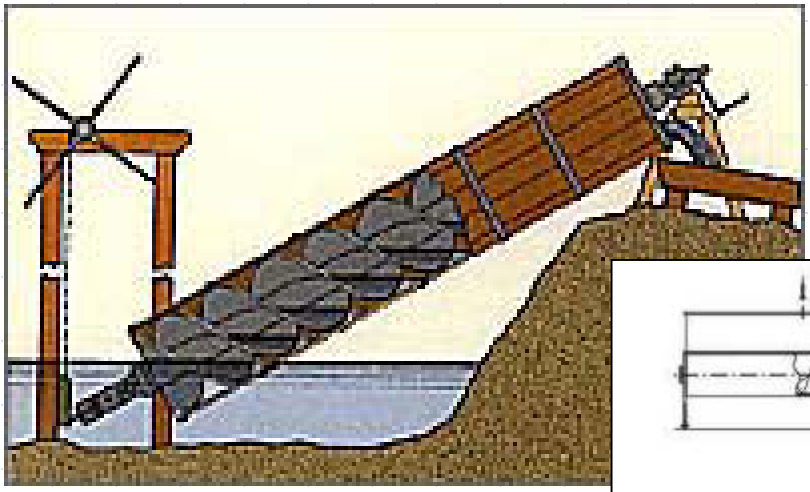
In-situ application:

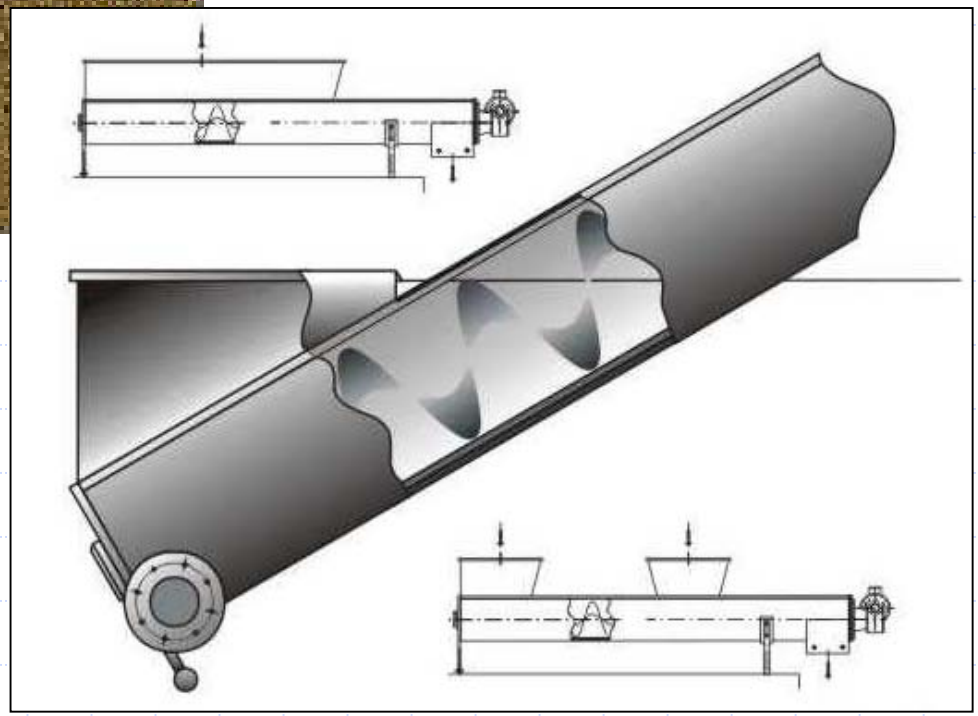


Ex-situ application - tanks:



Ex-situ application – screws:

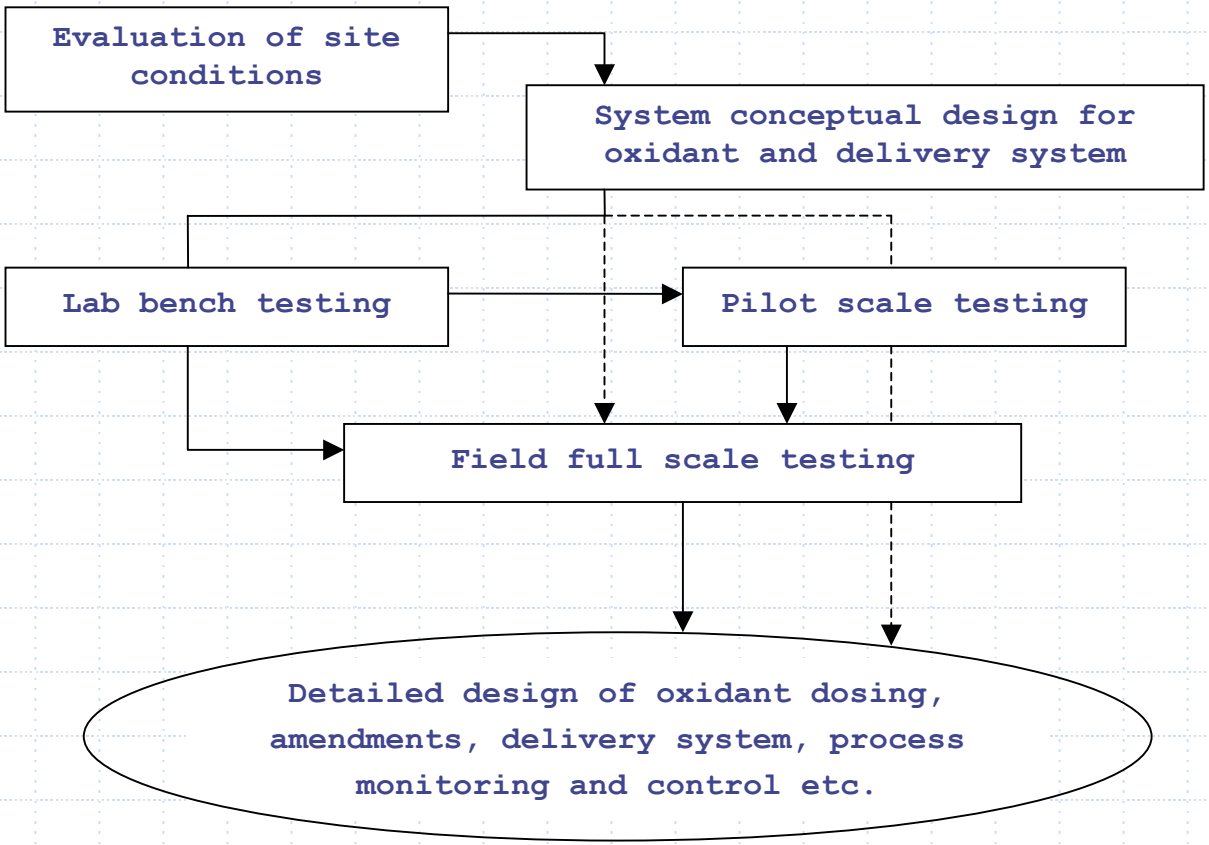




Pilot scale verification (2):

- Plans for pilot testing:
  - perform pilot on contaminated soil Milevsko
  - ex-situ application
  - June 2005
- Verification of chemical mass and its efficiency
- Determination of time for applying chemical mass
- Parameters: temperature, OPR, conductivity, pH
- Off-gas monitoring

Full scale application methodology:



Conclusions:

- Chemical oxidation seems to be suitable remedial approach for low-medium PCB concentrations

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- Selection of oxidation agent depends on:
  - contaminant type and concentration
  - treated matrix (water, soil)
  - geochemistry, hydrogeological parameters
  - other local conditions
- Before application necessary to carry out:
  - laboratory and pilot scale testing
  - full scale process and operating control

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