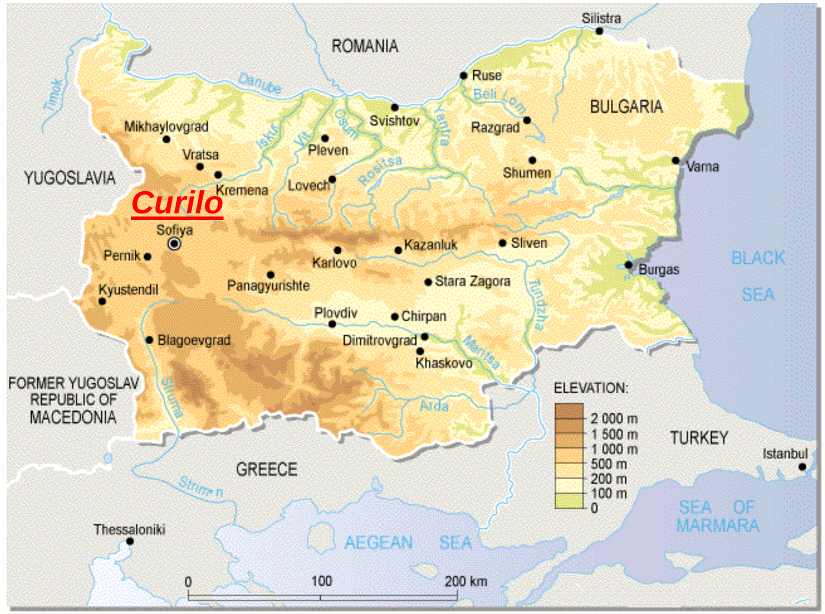
Update on MULTIBARRIER wall for acid mine drainage at curilo uranium mine



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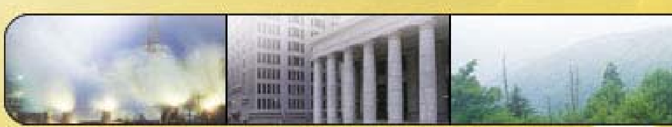
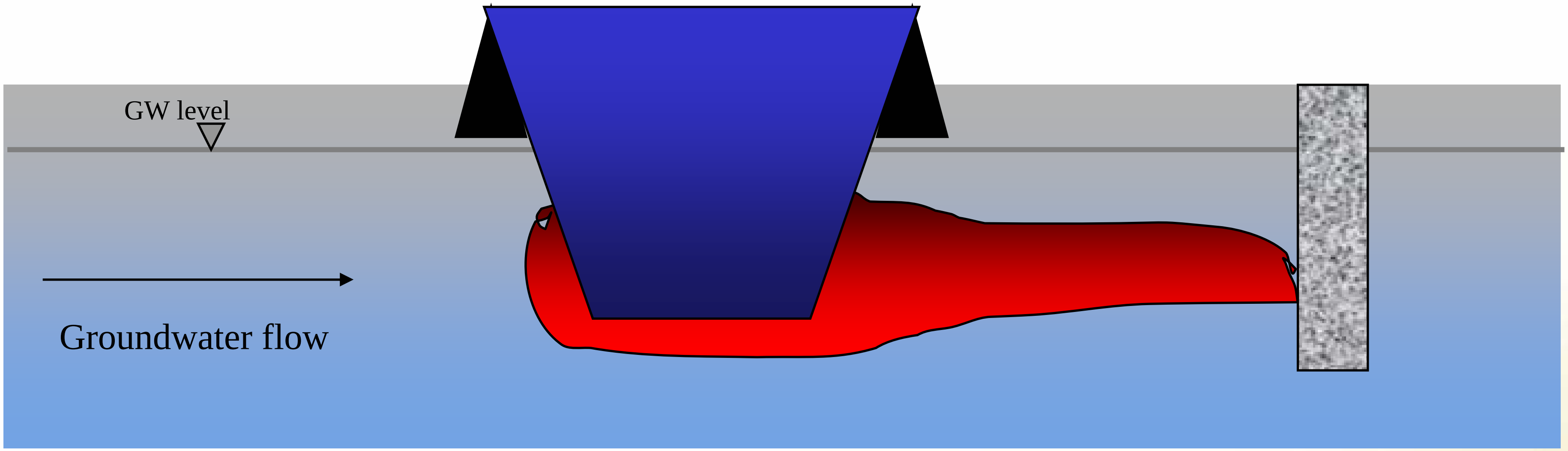
NATO – CCMS meeting, Ottawa, 12 – 15 June, 2005

Update on Multibarrier Wall for Acid Mine Drainage at Curilo Uranium Mine

- MULTIBARRIER definition
- Sequential versus mixed MULTIBARRIER
- Column and Container tests
- Pilot study at Curilo uranium mine in Bulgaria
- Conclusions



Landfill leakage: Multifunctional treatment zone or Multibarrier for removal of mixed pollutants



Evaluation of several combinations

- Chemical transformation (Fe°),
- Biotransformation (aerobic/anaerobic),
- Bioprecipitation
- Sorption

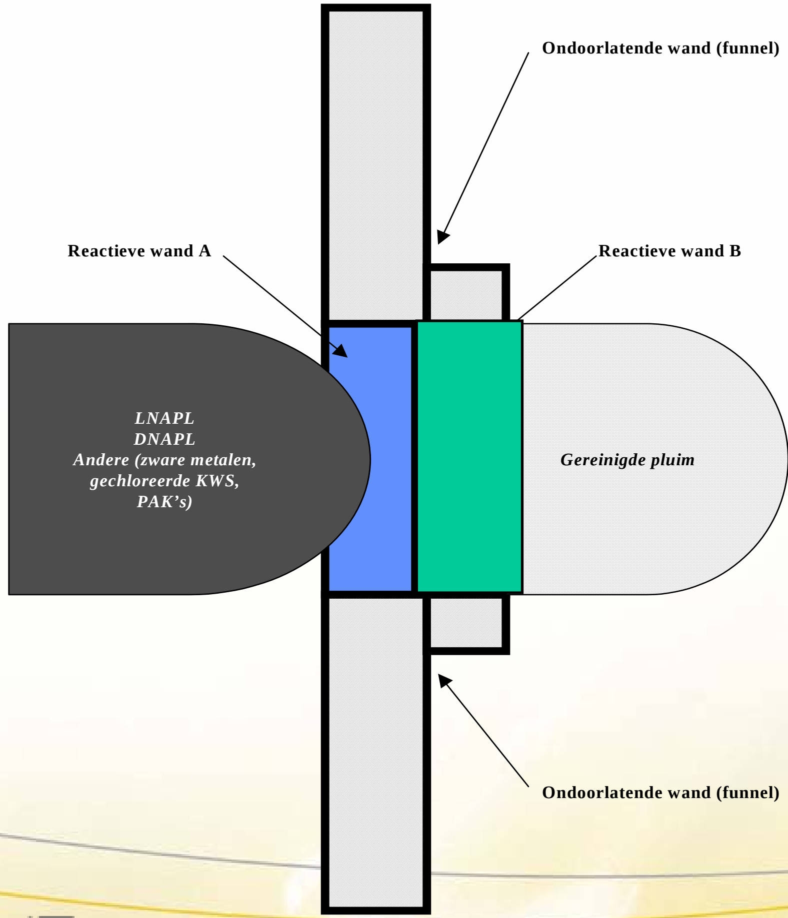
Two solutions:

-Installation of a new landfill (20 – 40 million EURO)

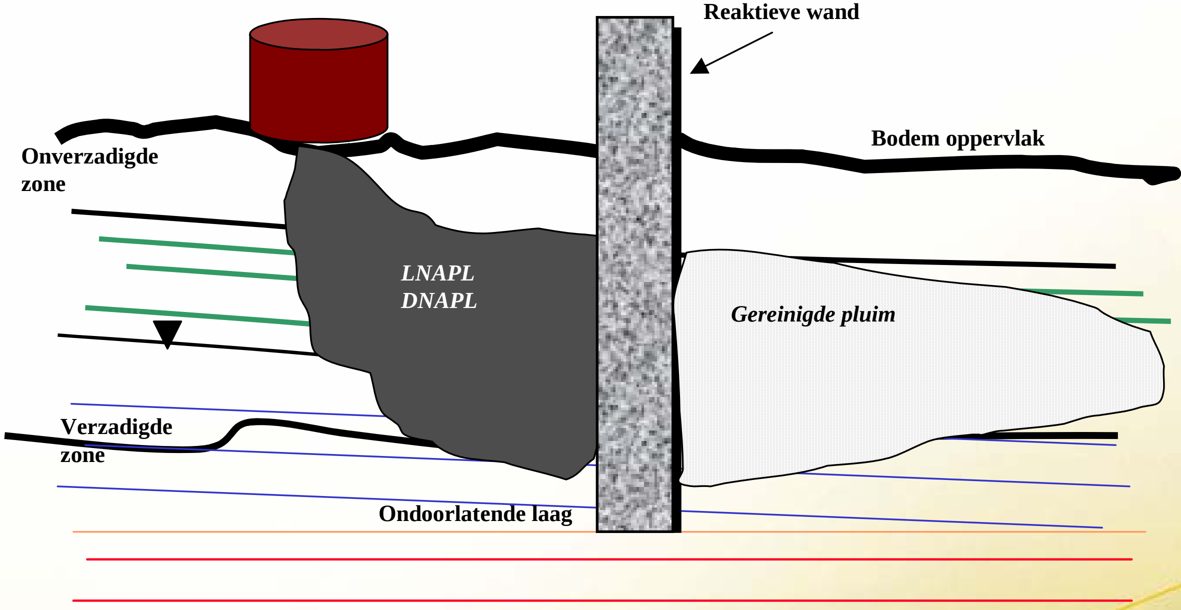
-Installation of a MULTIBARRIER (2 - 4 million EURO)

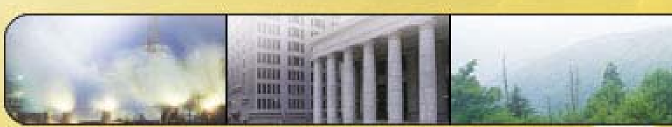
Sequential barrier vs mixed barrier

Sequential barrier



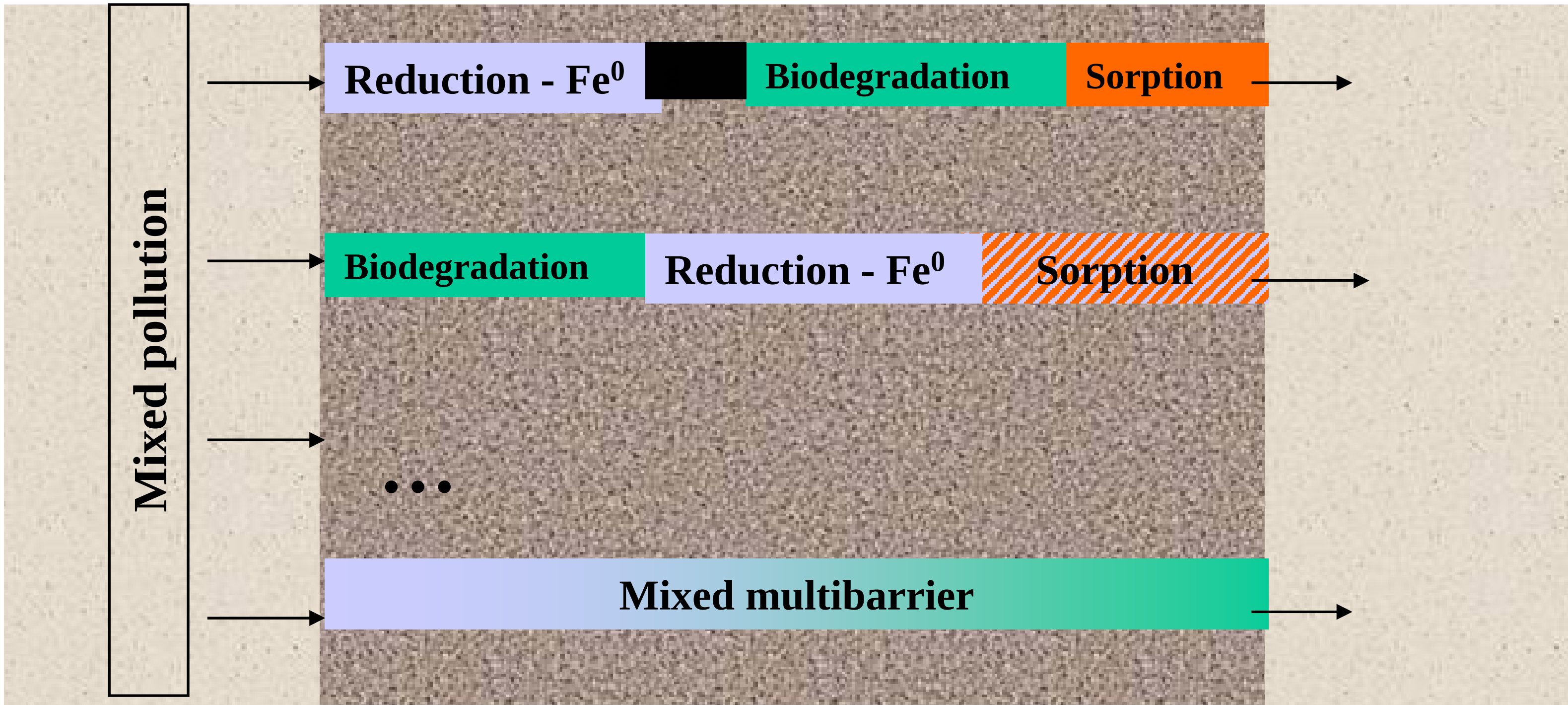
Mixed barrier



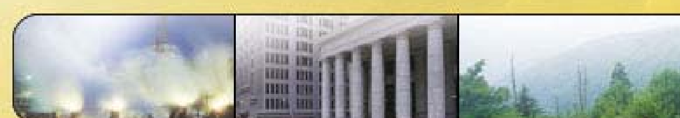


Design of multibarriers for mixed pollution

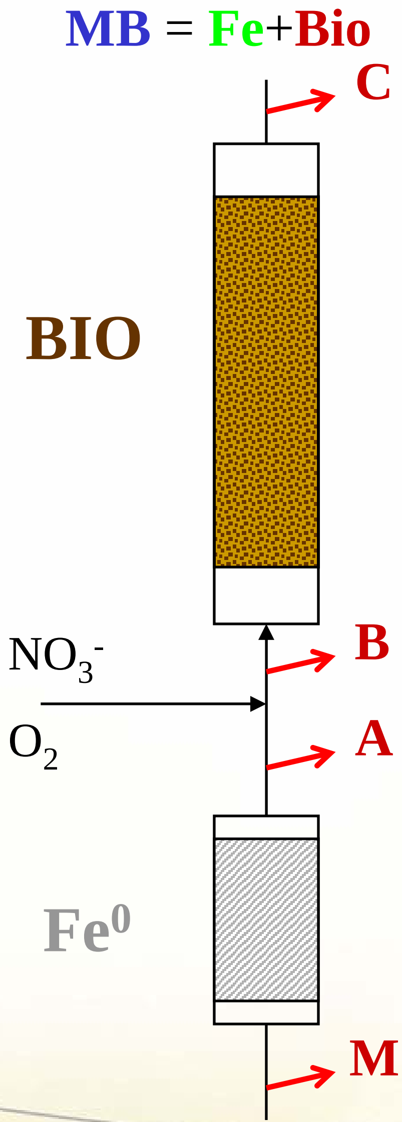
- Different multibarrier concepts:

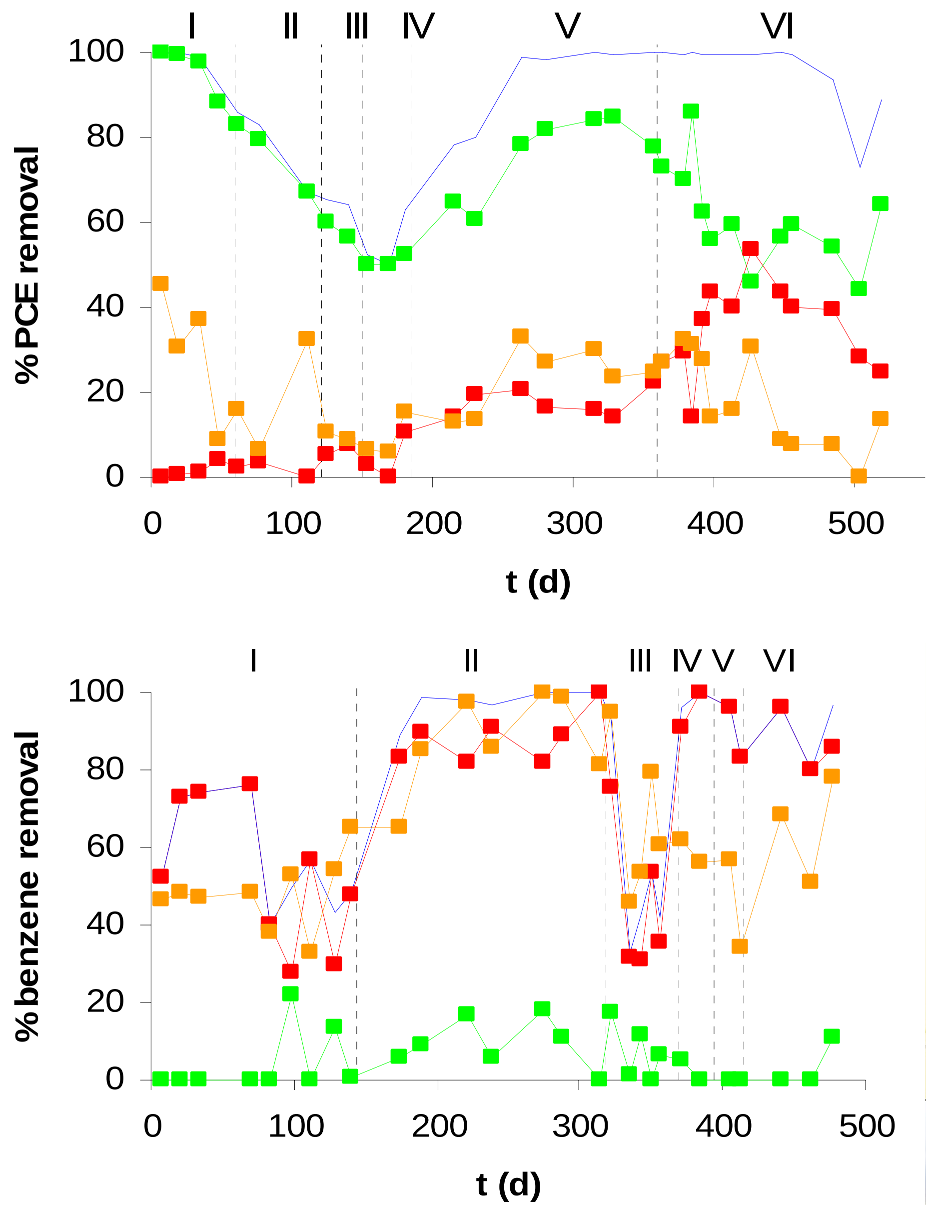


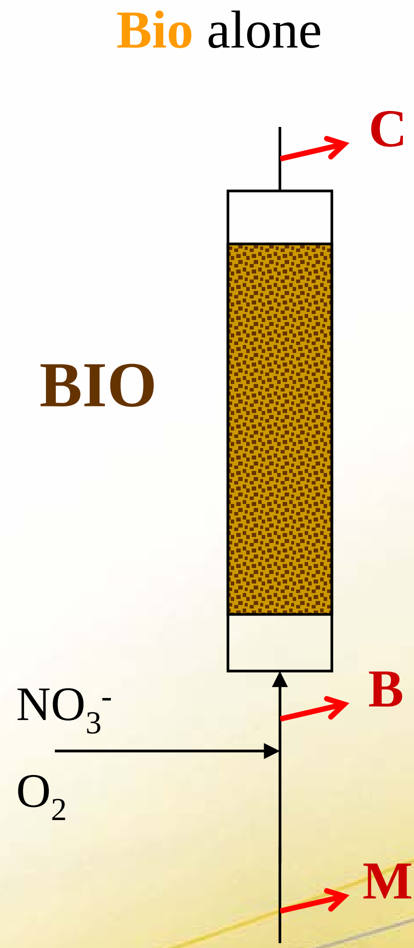
- Concept = Site specific and depending on the pollutants present



PCE removal in aerobic MB and benzene degradation in denitrifying MB







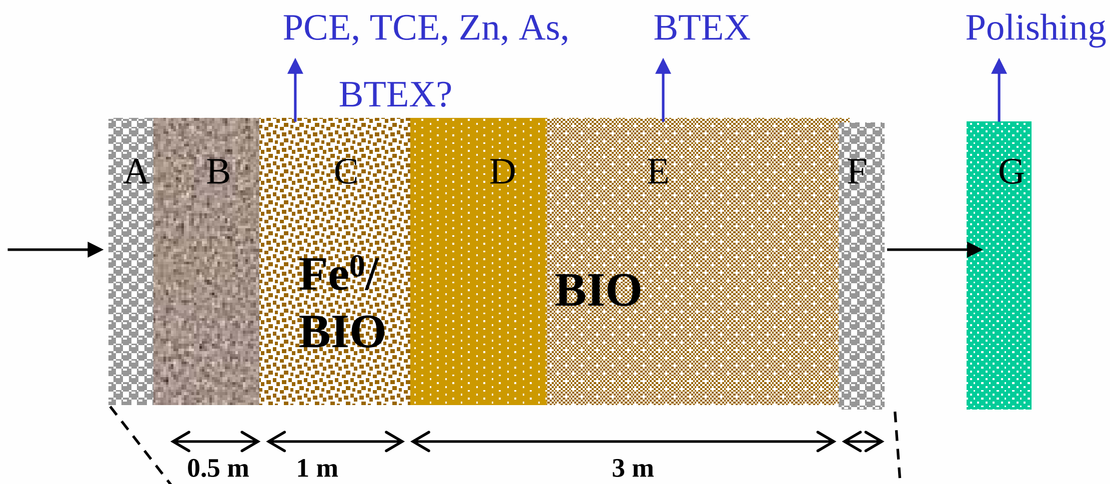
Mixed MULTIBARRIER system

Columns (L = 50 cm)
K1: test column
K2: abiotic control

Layers:
L1: FS/Aq = 78/22 (W)
L2: FS/Aq/Fe0 = 20/20/20 (W)

Removal of:
- PCE, TCE
- Benzene, Toluene
- Zn, As

Upscaling promising multibarrier concept



A: coarse zone (25 cm)

B: Aquifer material

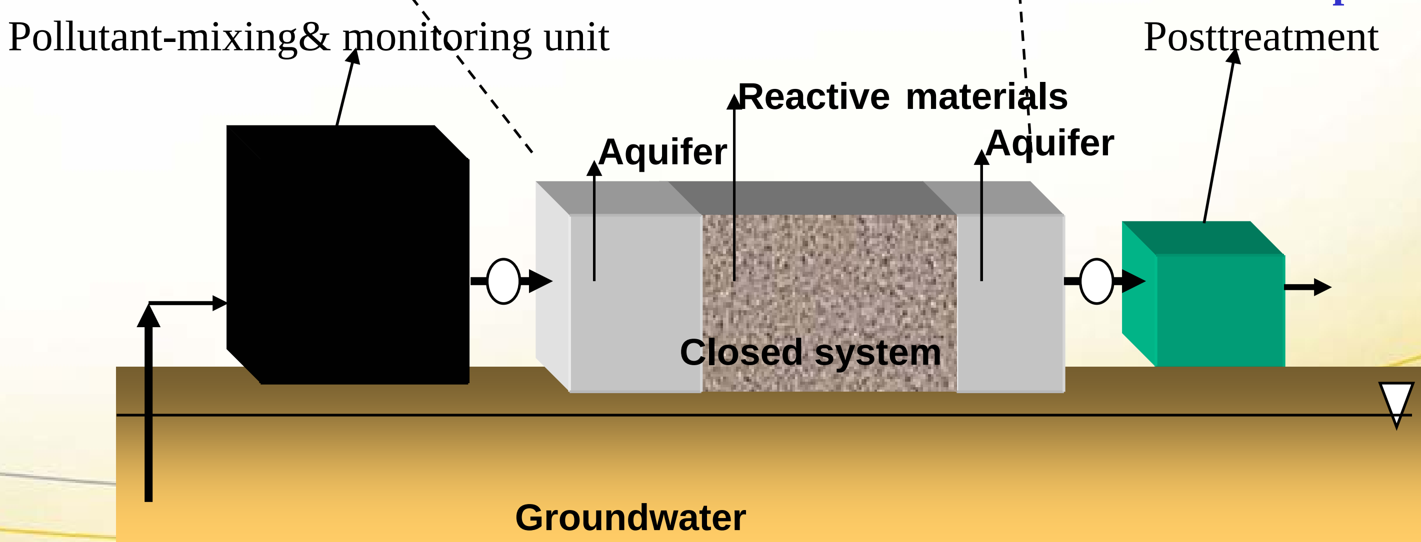
C: mixed Bio/Fe^0 barrier : FeA4/Aq/HM = 30/60/10

D: Biobarrier Aq/ HM (90/10)

E: Biobarrier Aq

E: coarse zone (25 cm)

F: Sorption barrier

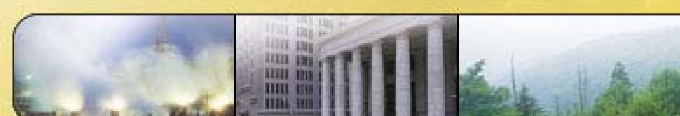


Set-up of MB at pilot-scale

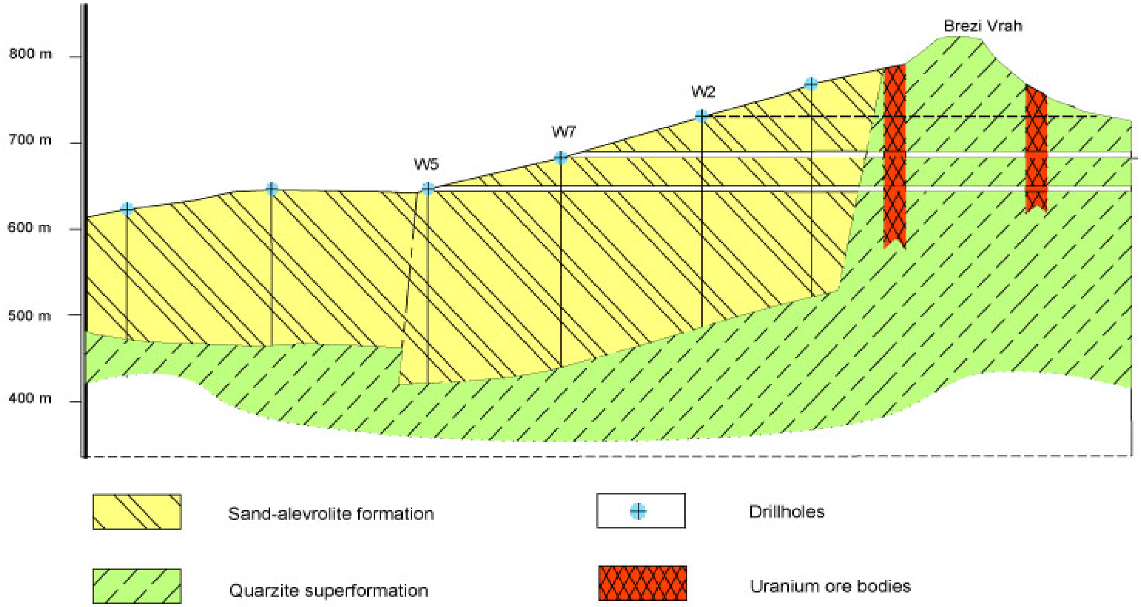
MULTIBARRIER systems

- Mixed pollution: PCE, TCE, B, T, mX, Zn, As

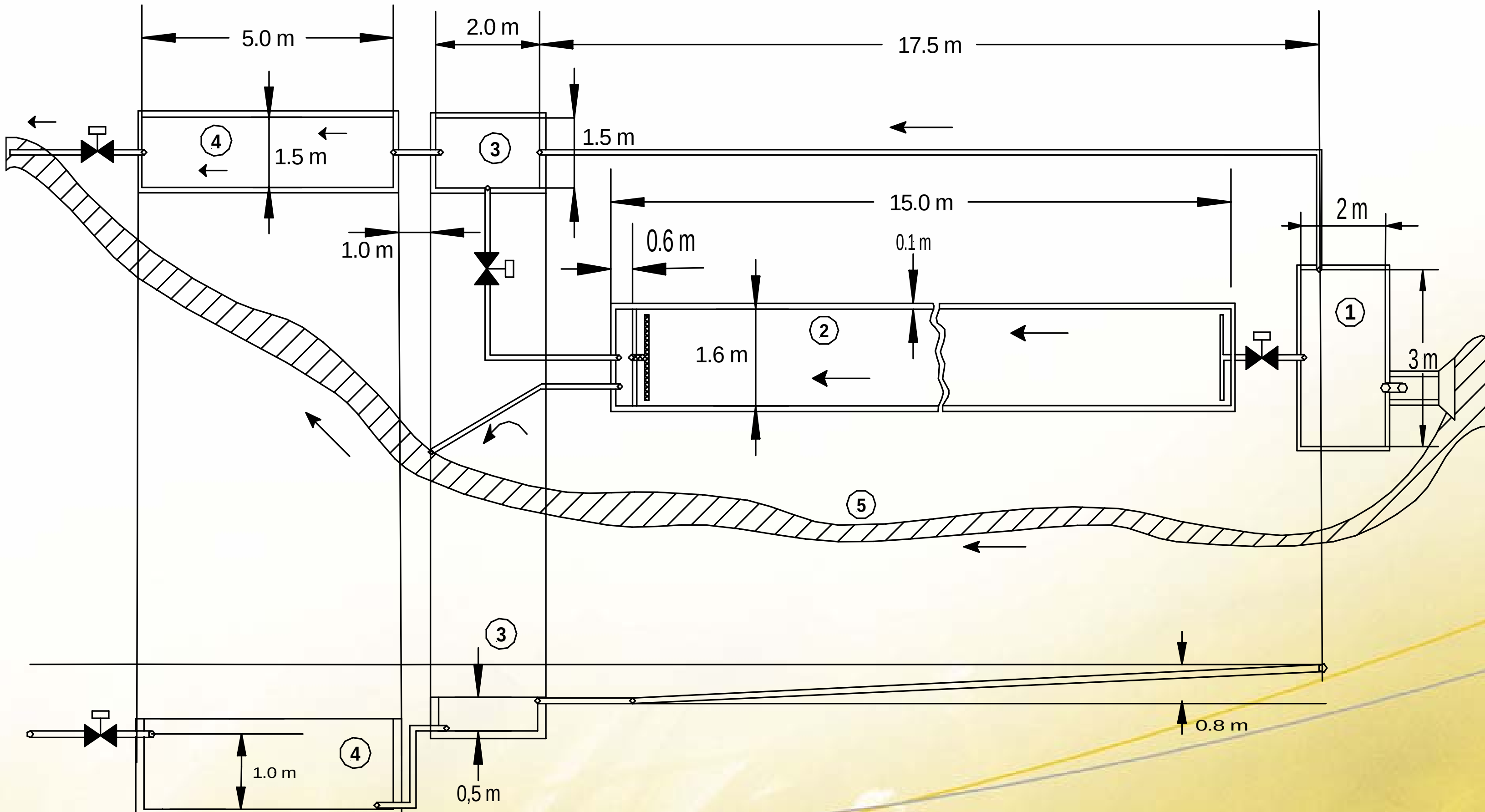
- Sequential Multibarrier: ZVI + Micro-aerofilic biobarrier
  - PCE, TCE dehalogenation in ZVI
  - Zn, As removal in ZVI
  - BTX degradation in biobarrier
  - No degradation of cDCE
- Sequential Multibarrier: ZVI + Anaerobic biobarrier (denitrifying)
  - PCE, TCE dehalogenation in ZVI
  - Zn, As removal in ZVI
  - T, X degradation in biobarrier
  - B partially degraded in biobarrier
  - No degradation of cDCE
- Mixed Multibarrier: filtersand, aquifer materiaal, ZVI + Anaerobic biobarrier in aquifer
  - PCE, TCE dehalogenation
  - Zn, As removal in ZVI
  - BTX degradation in mixed zone
  - No formation of cDCE or VC



Curilo deposit



Installation at Curilo deposit

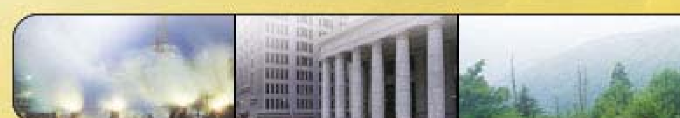


Curilo deposit: constructed wetland + sequential Multibarrier

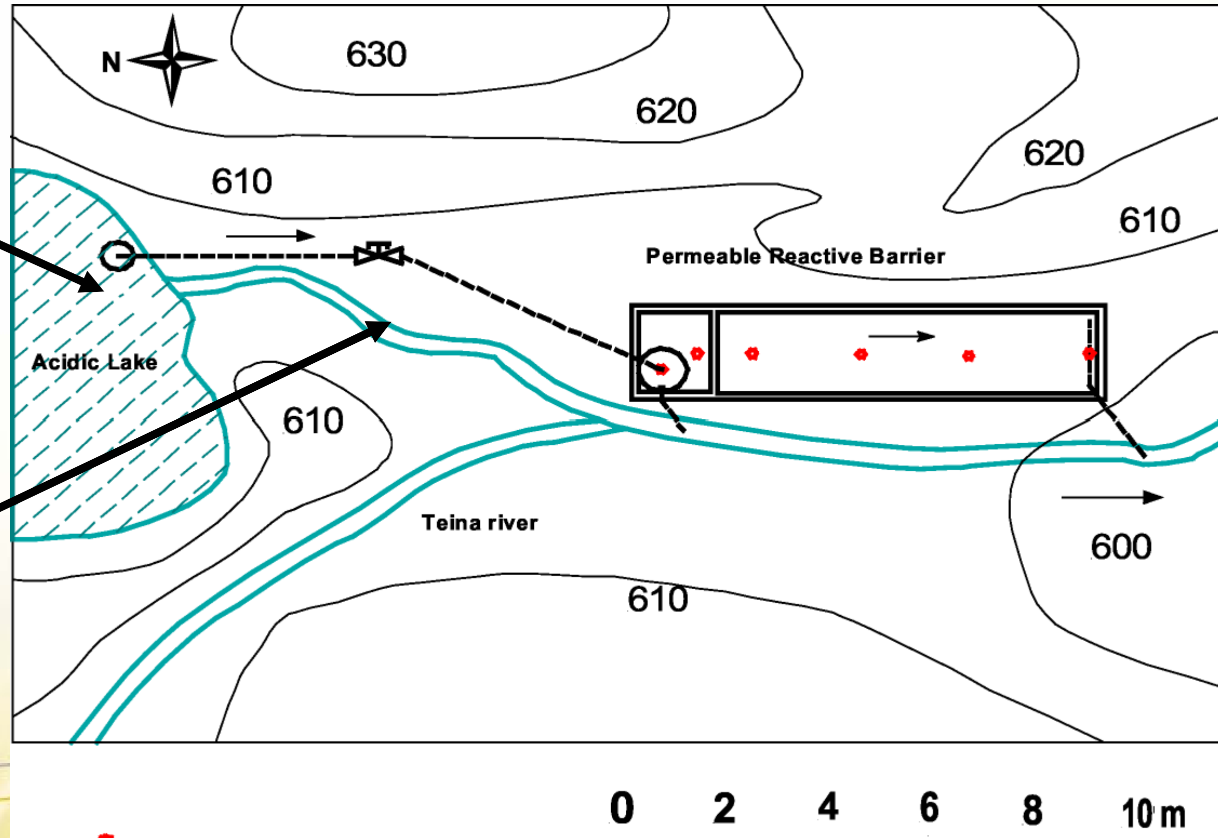
Effluent composition after sequential barrier system

Parameter	Content in the water			
	Before treatment	After barrier 1	After barrier 2	After barrier 3
pH	2.77 - 2.80	2.8 – 2.1	4.5 - 6.5	6.7 - 7.2
Eh, mV	(+460) - (+480)	(+510) - (+590)	(+252) - (+83)	(-206) - (-396)
TDS, mg/l	4250 - 4560	4200 - 3250	4100 - 3750	4300 - 2340
Acidity, mmol/l	23.0	19.00	4.1 - 1.0	-
Alkalinity, mmol/ l	-	-	0.2 - 2.1	9.6 - 22.1
Fe, mg/l	560	147.7	25.15	4.2
SO_4^{2-}, mg/l	3195	2610	2300	1780
Zn, mg/l	3.12	3.10	0.2	0.04
Cu, mg/l	11.5	6.76	1.59	0.003
Ni, mg/l	3.0	2.67	1.60	0.045
Co, mg/l	2.0	1.83	0.78	0.007
Mn, mg/l	30.0	29.55	26.1	6.85
Al, mg/l	121	118.60	71.30	0.52

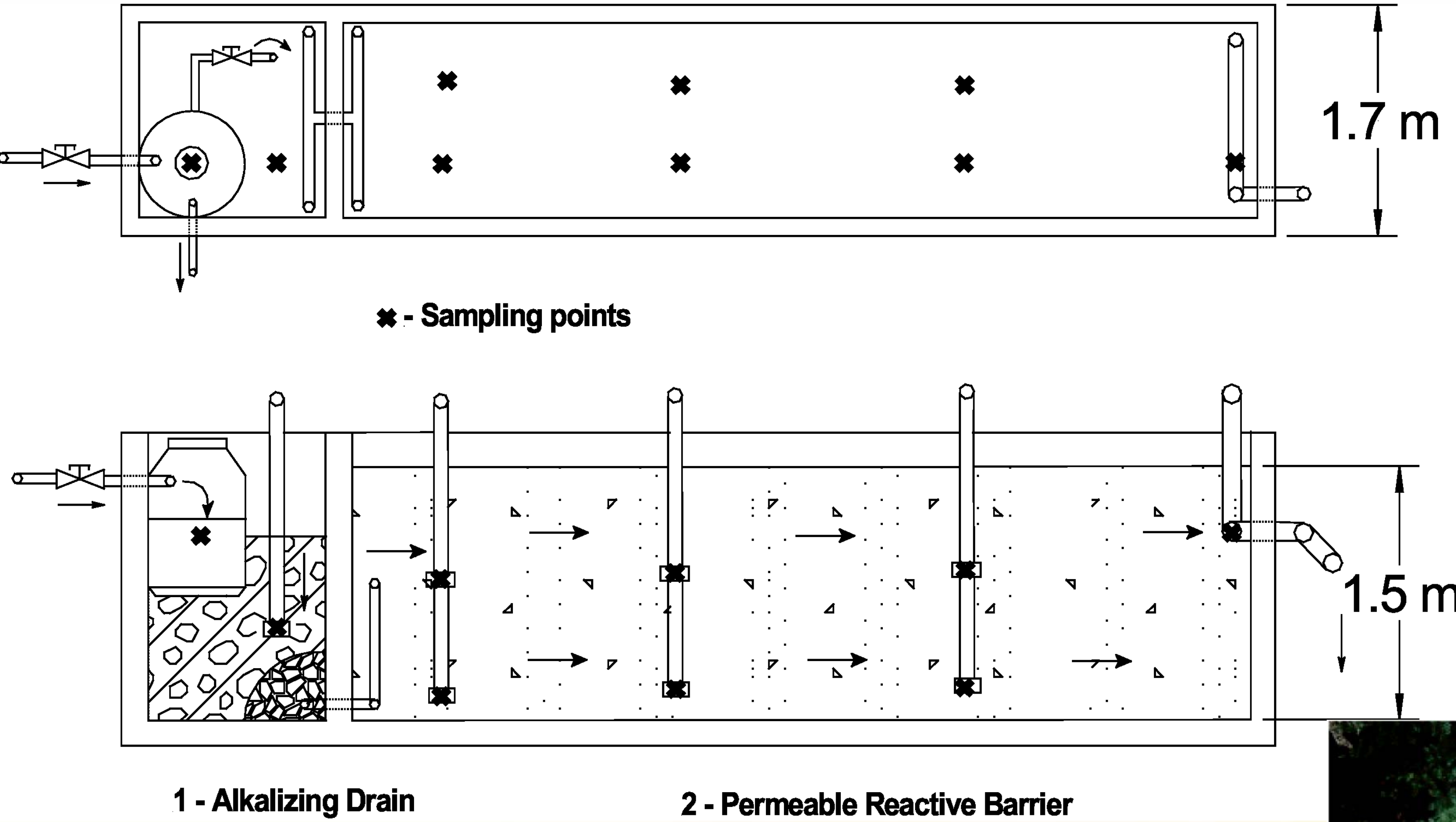
B-1 – oxidation of ferrous ions by acidophilic chemolithotrophic bacteria,
B-2 – chemical neutralization to about neutral pH without organic substrates,
B-3 – microbial sulphate reduction.



Mixed MULTIBARRIER on acid lake drainage



Mixed MULTIBARRIER on acid lake drainage

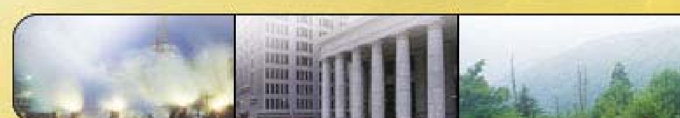


Limestone
Gravel

Cow manure, hay, straw,
Limestone, Zeolite-ammonium phosphate

Composition of the Mixed MULTIBARRIER

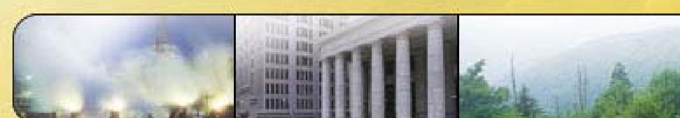
Component in the:	Dry weight, kg
Alkalizing Drain	800
Limestone	
Gravel	1700
Barrier for Microbial Dissimilatory Sulphate Reduction	
Cow Manure	6400
Hay	180
Straw	160
Limestone	2500
Zeolite saturated with ammonium phosphate	40



Results of MULTIBARRIER at Curilo site

Parameter	Acid mine drainage (inlet)	Alkalizing drain	Outlet
t°, C	1.4 - 2.6	1.1 - 2.3	3.8 - 4.0
pH	3.9 - 4.3	5.5 - 5.7	6.5
Eh, mV	(233) - (340)	(148)- (190)	(- 120) - (-140)
TDS, mg/ l	930 - 1970	915 - 1350	515 - 1950
Acidity, mmol/l	0.4 - 0.9	-	-
Alkalinity, mmol/l	0.1 - 0.3	2.1 - 2.8	8.4 - 15.3
DOC, mg/ l	-	-	82 - 186
Fe, mg/ l	4.9 - 6.2	1.1 - 1.9	0.09
Cu, mg/ l	0.82 - 1.2	0.1 - 0.7	0.05 - 0.08
Zn, mg/ l	0.68 - 1.25	0.12 - 0.24	0.04 - 0.09
Pb, mg/ l	0.10 - 0.25	0.11 - 0.20	< 0.04 - 0.06
Ni, mg/ l	0.17 - 0.23	0.06 - 0.13	0.02 - 0.06
Co, mg/ l	0.08 - 0.15	0.02 - 0.07	0.04 - 0.07
Cd, mg/ l	0.04 - 0.09	<0.004	<0.004
U, mg/ l	0.12 - 0.27	0.05 - 0.08	< 0.03
Al, mg/ l	4.2 - 5.6	0.9 - 1.4	<0.04 - 0.1
Mn, mg/ l	3.3 - 4.6	2.1 - 2.7	2.9 - 4.1
SO_4^{2-}, mg/ l	572 - 1240	624 - 856	260 - 980
HS^-, mg/l	-	-	0.5 - 0.8

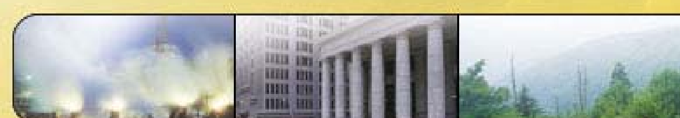
July – December 2004



Total Mass deposited in the MULTIBARRIER at Curilo site

	Alkaline	MB-1	MB-2	MB-3	MB-4
H^+	377.4	146.1	-	-	-
Fe	2320.2	338.7	93.3	65.3	104.6
Cu	152.1	369.5	7.6	17.8	2.7
Zn	48.7	50.3	26.9	29.9	5.3
Pb	2.1	12.2	8.7	4.7	0.2
Ni	21.8	51.3	11.5	7.4	3.2
Co	15.0	21.1	-	3.8	3.5
Cd	6.3	1.5	-	-	-
U	11.2	0.9	6.8	13.4	9.1
Al	4217.8	490.4	60	30.3	48.7
Mn	245.6	314.5	62.1	26	-
SO_4^{2-}	24328	40858	8726	23750	40383

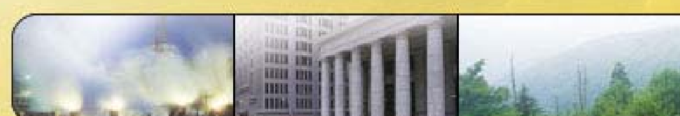
Total sum of the treated waters for the relevant periods – 297 800 l



Bacteria in AMD and MULTIBARRIER effluent

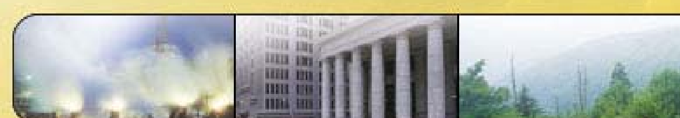
Microorganisms	In AMD	In barrier effluents
	CFU/ml	CFU/ml
Fe^{2+}-oxidizing chemolithotrophs (at pH 2.5)	10^5 - 10^8	0 - 10^1
Aerobic heterotrophs (at pH 2.5)	10^2 - 10^5	0 - 10^1
$S_2O_3{}^{2-}$-oxidizing chemolithotrophs (at pH 7)	0 - 10^2	10^2 - 10^4
Aerobic heterotrophs (at pH 7)	0 - 10^2	10^1 - 10^4
Anaerobic heterotrophs (at pH 7)	0 - 10^1	10^4 - 10^7
Sulphate-reducing bacteria	0 - 10^1	10^5 - 10^8
Cellulose-degrading microorganisms	0 -10^1	10^3 - 10^7
Bacteria fermenting sugars with gas production	ND	10^4 - 10^7
Ammonifying bacteria	ND	10^2 - 10^5
Denitrifying bacteria	ND	10^2 - 10^5
Fe^{3+}-reducing bacteria	ND	10^3 - 10^6
Methane-producing bacteria	ND	10^1 - 10^4

Note: ND = not detected



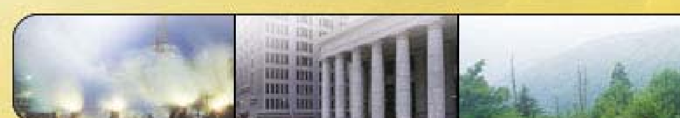
Sulphate Reducing Bacteria in Multibarrier effluent

Sulphate-reducing bacteria	**CFU/ml**
Desulfovibrio **(mainly *D. desulfuricans* and *D. vulgaris*)**	**10^4 - 10^7**
Desulfobulbus **(mainly *D. elongatus*)**	**10^3 - 10^7**
Desulfococcus (D. postgatei)	**10^2 - 10^5**
Desulfobacter (D. multivorans)	**10^3 - 10^7**
Desulfobacterium (D. autotrophicum **and some non-identified**	**10^1 - 10^4**
Desulfotomaculum **(mainly *D. nigrificans*)**	**10^1 - 10^4**
Desulfosarcina (D. variabilis)	**10^2 - 10^5**
Desulfomonas **(non-identified species)**	**10^1 - 10^4**



Metals on different fractions in MULTIBARRIER

Pollutants	Portions of pollutants in different mobility fractions, %			
	Exchangeable	Carbonate	Oxidizable	Reducible
U	8 – 32	2 – 6	68 - 87	2 – 5
Ra	71 – 84	5 - 12	1 - 5	5 – 14
Cu	10 – 25	8 – 14	64 - 80	3 – 7
Mn	7 – 16	4 -10	1- 4	73 – 87
Fe	5 - 15	3 - 10	68 - 84	3 - 9



Conclusions

- Sulphate Reduction process is most important for metal removal
- Addition of limestone, Fe° or zeolites-ammonium phosphate improves the process
- Mn removal can be obtained only after an aerobic second step barrier (removes also DOC)
- AMD at pH >2, better pretreatment with Limestone
- Pretreatment with limestone is efficient in Fe^{2+} removal, and more efficient than bacterial oxidation of Fe^{2+} to Fe^{3+}
- Final process is alkalizing drain + Sulphate Reducing Barrier improved with Fe° and zeolites-ammonium phosphate
- Still limited sulphate removal
- Radioactivity reduced from 4 Bq/l to < 0.05 Bq/l
- ISBP-process is an alternative