Remediation on the former uranium mining and milling site (Hungary): Case Study

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The presented work is a common work of the experts from
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and
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and other companies, institutions

„DIFPOLMINE” CONFERENCE Budapest
4-8 July 2005
The site has a close connection with drinking water catchment areas (T and P).

Water treatment is necessary for:
- Mine water
- Contaminated groundwater
Geological cross-section of the former mining site (Western Mecsek)

Legend:
- **Sandstone**
- **Claystone**
- **P-T Sandstone**
- **Anhydrite**
- **Siltstone aquitard**
- **Uranium ore**
- **Drinking water aquifer (D)**
- **Loose sand (aquifer)**
- **Tectonic zone**
- **M Sand and clay**

Anticline

Southern shaft

Northern shafts

Adit

D- drinking water aquifer
Water treatment processes

1) Mine water treatment
   Anion-exchange process is used for U
   (TDS~1.6 g/l; U~5 mg/l; As<12 mg/l, Ra~0.3 Bq/l)

2) Groundwater treatment
   Pump and treat process
   (TDS~3-15 g/l; U<0.1 mg/l; Ra~0.08 Bq/l)
   Heavy metals: As<12 mg/l;
   Pilot-scale PRB (ZVI + sand mixture)
   (in situ groundwater treatment, experiment)
I Mine water treatment station

Station is situated on the area of former Shaft NI
Yellow cake production

Precipitation of uranium peroxide

U-concentrate accretion on the mixer in dryer causes some problems

Packing unit
Mine water treatment

Sorption efficiency for uranium

- $U_{\text{in mine water}} \approx 7 \text{ t/a}$
- $U_{\text{effl.}} \approx 2 \text{ t/a}$
- $V_{\text{extra water from remediation activity of HL}} \approx 1.2 \text{ Mm}^3/a$
- $V_{\text{effl.}} \approx 0.44 \text{ Mm}^3/a$
- $U_{\text{effl.}} \approx 0.2 \text{ mg/l}$
The change of uranium concentration in mine water over long period (1968-2005)

Volume and concentration were affected by heap leaching

6-7 mg/l 35 years 4.5-5 mg/l
II Groundwater treatment
Tailings Ponds

Total volume of the tailings:
20.4 kt solid + 32 Mm³ of liquid
Groundwater restoration

TDS (mg/l) in the shallow groundwater around the tailing ponds in 2003

TDS (mg/l) in the deeper groundwater around the tailing ponds in 2003

GW contamination

Shallow GW 5-20 m
Deeper GW 25-40 m

5-20 m

25-40 m

18 g/l

4 g/l

1000 4000 8000 12000 16000 20000
0 500 1000 1500 2000

S hallow GW 5-20 m
Deeper GW 25-40 m

TPI

TPII

TDS

1000 4000 8000 12000 16000 20000
0 500 1000 1500 2000
Groundwater contamination under the TP

TDS in pore water

Depth, m

TDS, mg/l

0 5000 10000 15000 20000 25000 30000

0 -5 -10 -15 -20 -25 -30 -35 -40

0 5000 10000 15000 20000 25000 30000
Groundwater treatment process

Shallow GW: TDS~10-12 g/l
   For treatment
Deeper GW: TDS~3-5 g/l
   Direct discharge

Treatment process consist of:
   • Precipitation of magnesium and gypsum with calcium hydroxide
   • Sedimentation and thickening
   • Filtration
Groundwater extraction system

Drainage: 2.8 km
Wells: 15+12
Q~0.5 Mm³/a
0.3 Mm³/a
Sludge from treatment

**Sludge**

7kt/a (with 50% water content)

**Treated water:** ~0.36 Mm³/a

TDS~6-7 g/l (retention time!!)

(NaCl~3 g/l)

- Mg~17%
- Ca~17%
- SO4~26%
- U~60-70 g/t
- Ra~24 Bq/kg
Gypsum accretion on the surface of technological equipment

Critical parts and units must be monthly cleaned from gypsum accretion
Water discharge summary

**Treated groundwater**
- V: 0.36 Mm³

**Treated mine water**
- V: 0.44 Mm³

**Mixing basin**
- TDS: 3.2 g/l
- U: 0.2 mg/l
- Ra: 0.18 Bq/l

**Non-treated water** (e.g. deeper GW)

**Receiver**

Data for 2004
Field test aiming at investigating of long-term performance of PRB (EU project: EVKI-1999-00035) for removing of U from GW

Practical solutions are known in first of all in USA, but the long-term performance is still under investigation

For field test ZVI+sand mixture was selected, though different reactive materials were tested in laboratory and in columns on the field
Permeable reactive barriers
Permeable reactive barriers

Landfill Liner

Trench and Fill

Chemical Barrier

Flow

Waste

Contaminant Plume

Trench (filled)

Flow

Aquifer

Chemical Barrier
Funel anf gate system
Uranium contaminated groundwater in valley Zsid.

Slite contamination of GW was detected in GW on the site.
Laboratory experiments in columns

Iron, hydroxiapatite, anion exchange resin, etc. were tested
Removal of uranium from contaminated GW

Uranium can be is removed from GW by steel fibres

Feed Hb1/1

Effluent

Sample number
Changing the general chemistry of water

By carbonate calcium etc. Are dropps during treatment

Sample number

Feed Hb1/1

k concentration, mg/l

Ca

Mg

HCO3
Columns in monitoring wells

- Plastic pipe
- Ditch
- Column $F=8-12cm^2$, $L=1-1.4m$
- $\Delta H$

Drain
Field column experiments
Geochemical processes controlling GW chemistry

\[ \text{H}_2\text{CO}_3 = \text{HCO}_3^- + \text{H}^+ \]
\[ K = 10^{-6.3} \]
\[ \text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+ \quad K = 10^{-10.25} \]

\[ [\text{Fe}][\text{CO}_3] = 2.50 \times 10^{-11} \quad 20^0\text{C} \]
\[ [\text{Fe}][\text{OH}]^2 = 1.64 \times 10^{-14} \quad 18^0\text{C} \]

\[ [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 1.20 \times 10^{-8} \quad 20^0\text{C} \]
Geochemical processes in GW

Iron concentration vs. pH

Fe$^{2+}$ + CO$_3^{2-}$ = FeCO$_3$

Fe, mg/l
The installation is located in a narrow valley at the foot of WPIII, linking the mining area with drinking water aquifer (Zsid-valley).
Principal design of the experimental PRB

Cross-section A-B

Legend:
- Orange: Sand
- Gray: 0.39 t/m³ iron (1-3 mm, 5 t) with sand
- Black: 1.28 t/m³ iron (0.2-2 mm, 33 t) with sand
- White dot: Mon. wells

Up stream

Down stream

Soil 50 cm
Comp. clay 30 cm
HDPE

2.5 m
3.8 m
6.8 m

Bentofix
Bedrock
Elemental iron mixed with sand

Spec. Surface:
0.7 $m^2/g$

0.2-3 mm
Construction of the PRB

Permian sandstone with sediments

Two layers of Fe+sand mixture
Monitoring wells placed in reactive zones
Construction of the PRB

Design of experimental Permeable Reactive Barrier

- Course ZVI + sand
- ZVI + sand
- Sand
- Clay
- Aquifers

Length: 6.8 m; Depth: 3.9 m
Width: 1.5 m;
Two zones;
G: 39 t ZVI (mixed with sand)
PRB with monitoring wells

28 monitoring wells
Precipitation of uranium and dissolution of iron

Uranium concentration profile in the PRB

Iron concentration profile in the PRB

Iron first dissolves in first zone than precipitates in the 2nd zone

Uranium conc. drops in the first zone
Concentration profiles in zones of PRB

- Ca
- Mg
- TDS
- SO4
- HCO3
- Spec. cond.

Fe~20 mg/l
TDS

% from inflow vs width of PRB, m
Uranium is removed with high efficiency but huge volume of inert compounds (CaCO₃, MgCO₃ etc.) is precipitated.
Isolines of uranium and calcium concentrations on the test field
V.7 Development of uranium concentration in downstream monitoring well

Uranium concentration in groundwater after construction of the PRB

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Const. of PRB
Performance change

Water passed through the PRB: ~700 m³/a
Formed precipitate: ~0.5 kg/m³ ~ 350 kg/a
Free porosity in PRB (original) ~11 m³
Annual losses: ~0.35 x 2.7 ~ 0.094 m³
  in percentage: ~1-1.5%

Iron dissolution: ~20-30 mg/l Fe(II)
  G = ~700 x 0.03 = 21 kg/a
Performance monitoring is continued
• by regular water sampling
• by planned drillings
• by hydrogeological evaluation
The research works related to the GW treatment was supported by the IAEA (Contract: N° 9114).

The research related to the PRB and dispersion of contaminants under TPs was partially supported by EU (Contract: EVIKI-1999-00186 and EVGI-CT-2002-00035)
Precipitation of gypsum and magnesium

Kinetic curves of the precipitation of magnesium hydroxide and gypsum

- Concentration, g/l vs. Time, hours
- Graph showing the concentration of calcium (Ca) and magnesium (Mg) over time.
I.3 Project cost distribution

A Beruházási Program létesítményi sorainak költségeloszlás diagramja

- TPs: 40%
- Mines: 13%
- Res.fund: 5%
- Roads: 8%
- HL: 4%
- MWT: 6%
- 11%
- 4%
- 1%
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