Effects of CO_2 leakages from storage sites on the quality of potable groundwater

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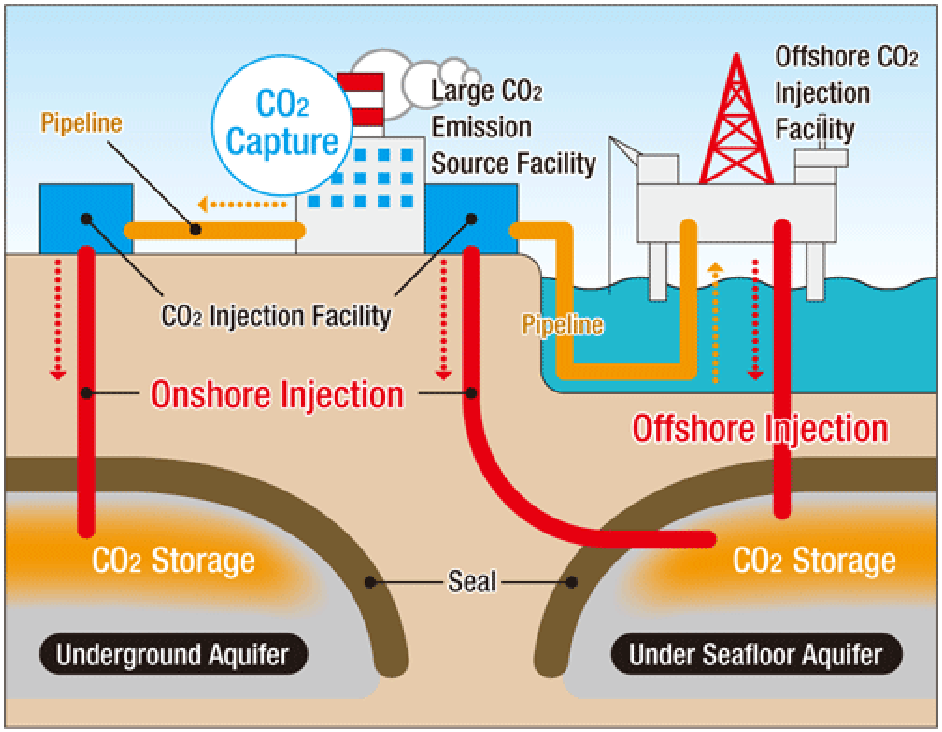
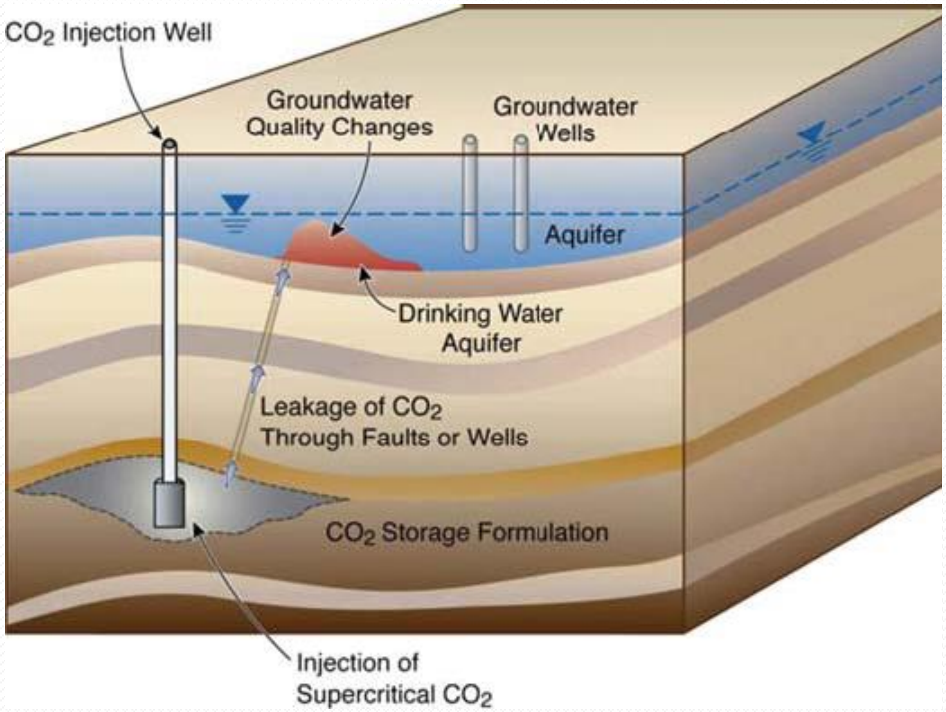
Capture and Storage of CO_2



- The annual emission of CO_2 has increased by 80% between 1970 and 2004, and the rate of CO_2 emission increase was much higher during the period 1995-2004 (0.92 Gt/yr) compared to the period 1970-1994 (0.43 Gt/yr)
- In order to keep the CO_2 concentration below 500 ppm and limit climatic changes, compared to the concentration level of 1990, the emissions of CO_2 must be reduced by 30% until 2020 and by 50% until 2050.
- The capture of CO_2 emissions and subsequent emplacement of supercritical CO_2 into geological media is the most well-promising technology of CO_2 sequestration. Examples of geological media: saline aquifers, depleted oil/gas reservoirs, and coal formations.
- Deep saline aquifers have a huge storability ~ 400 Gt – 10000 Gt CO_2 and the financial viability of CO_2 in such reservoirs has already been demonstrated.

Description of the problem



Apps et al., Transp. Porous Media 82, 215-246 (2010)

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}$$

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_{3(aq)}$$

$$H_2CO_{3(aq)} \leftrightarrow HCO^-_{3(aq)} + H^+_{(aq)}$$

$$HCO^-_{3(aq)} \leftrightarrow CO^{2-}_{3(aq)} + H^+_{(aq)}$$

- **CO_2 leakages from storage sites may occur through activated faults and abandoned wells**
- **Reduction of solution pH and groundwater / CO_2 / solid interactions may stimulate the release of hazardous trace elements (e.g. heavy metals) from the solid surface to the aqueous phase**

$$MeO_{(s)} + 2H^+ \leftrightarrow Me^{2+} + H_2O$$

- **High concentrations of heavy metals in potable groundwater lead to degradation of its quality**
- **Earlier studies have placed emphasis on batch tests and development of macroscopic (aquifer-scale) geochemical models**
- **There is a lack of fundamental experimental studies and mesoscopic numerical model (soil column-scale) under flow-through conditions**

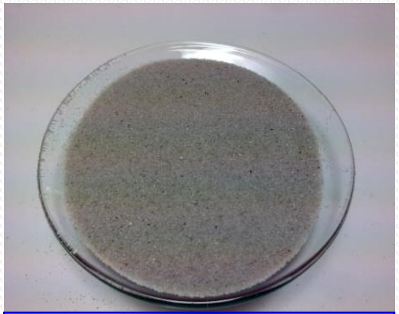
Presentation Outline

- Porous medium model
- Experimental Procedure
- Results and Discussion
- Supplementary batch experiments
- Numerical Model
- Conclusions

Porous Medium Model

Soils

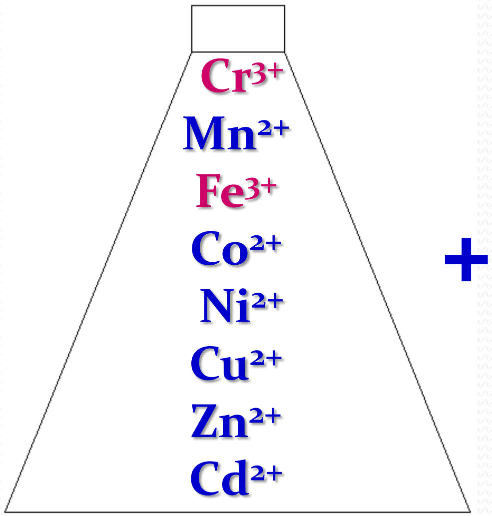
- Minerals
- Metal Oxides
- Organic Matter



Silica Sand

(125-250μm)

+



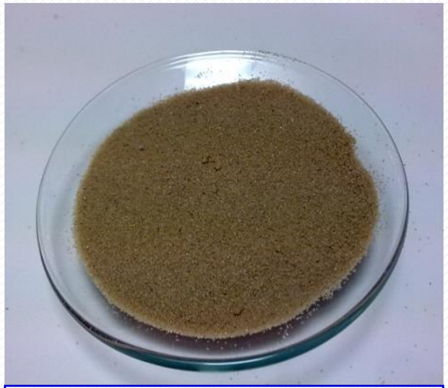
Aqueous solution of nitrate

+

Gently stir for 1 week

pH adjust with solution 1M NαOH

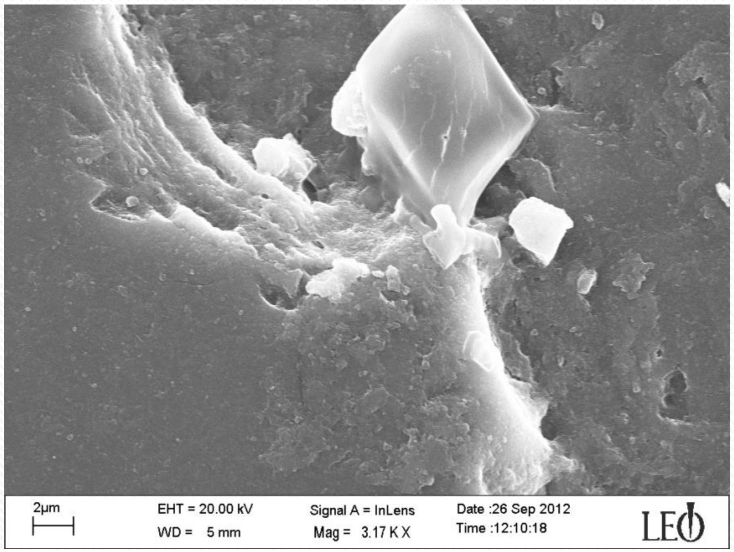
Drying

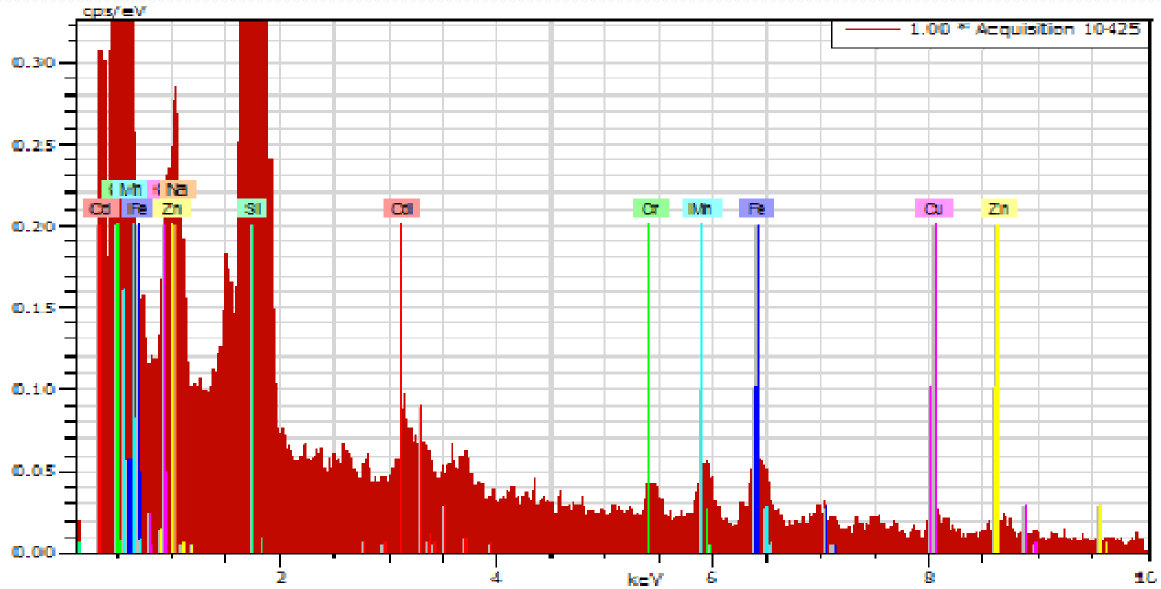


Treated Silica Sand

Metal Precipitation

Scanning Electron Microscopy – Energy Dispersion Spectroscopy (SEM – EDS)





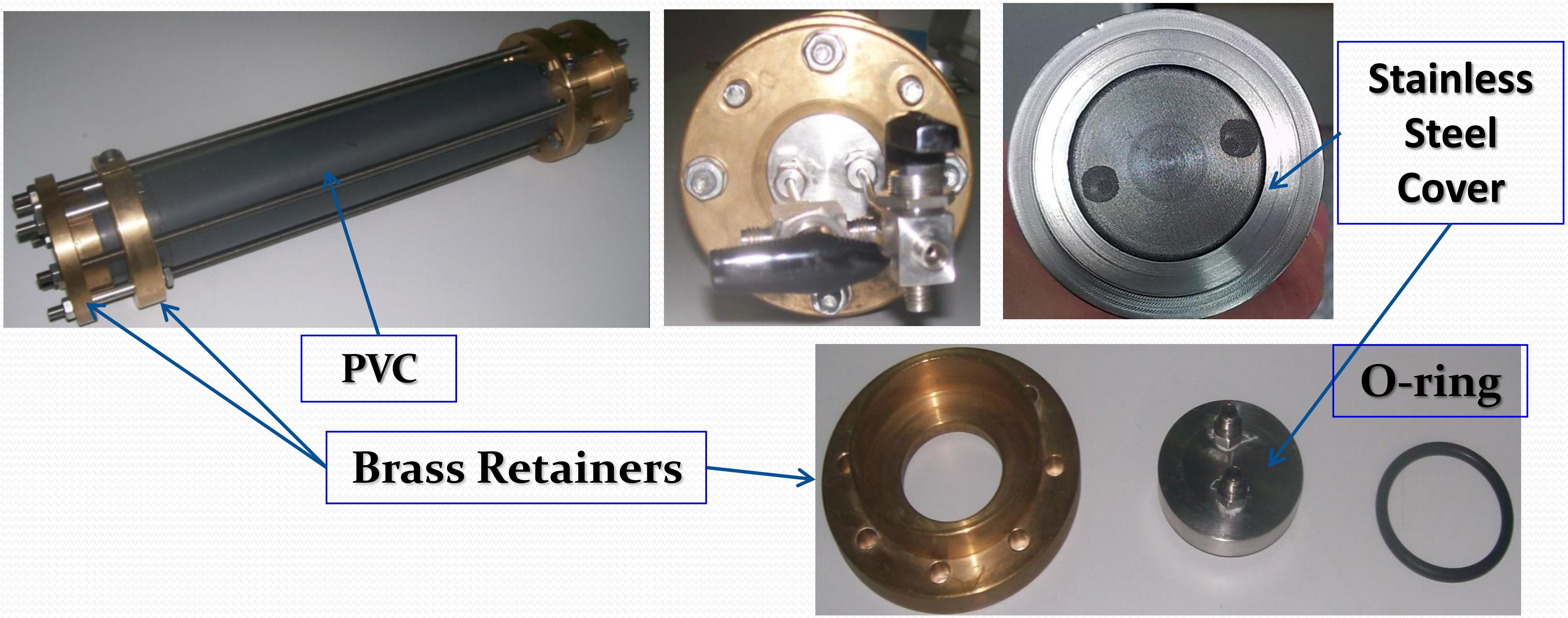
Quantitative Analysis with Atomic Absorption Spectroscopy (AAS)

Flame Atomizer: *High heavy metal concentrations*

Electrothermal Atomizer –Graphite Tube: *Low heavy metal concentrations*

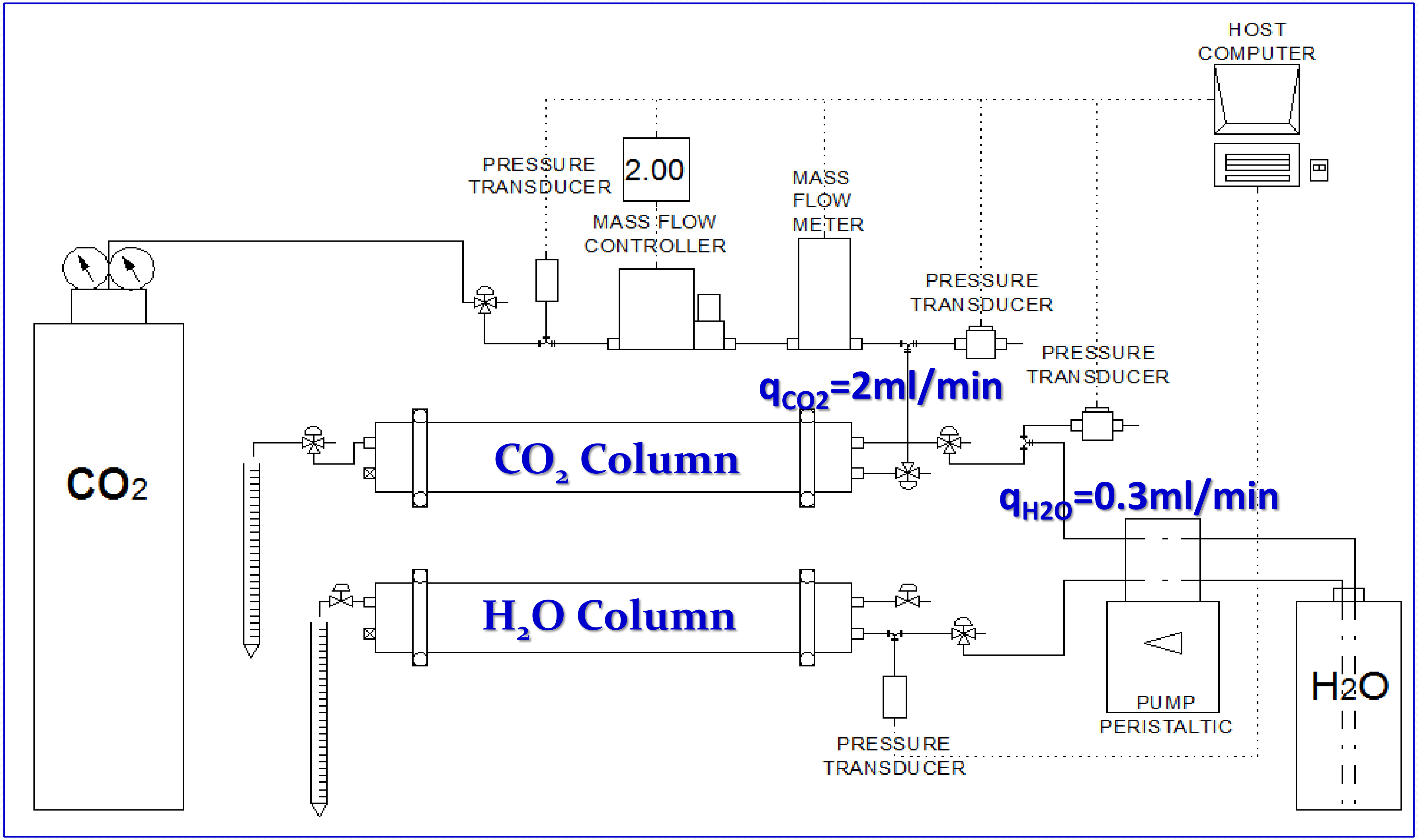
Element	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd
mg/g-sand	0.072	0.069	0.224	0.036	0.053	0.108	0.0675	0.0725

Sand Column Properties



Characteristics		
Construction Material	Column	PVC
	Retainers	Brass
	Cover	Stainless steel
Column Dimensions (Length X Diam)	40 cm x 3 cm	
Sandpack Permeability	26.5 D	
Sand Grain Sizes	125-250 μm	

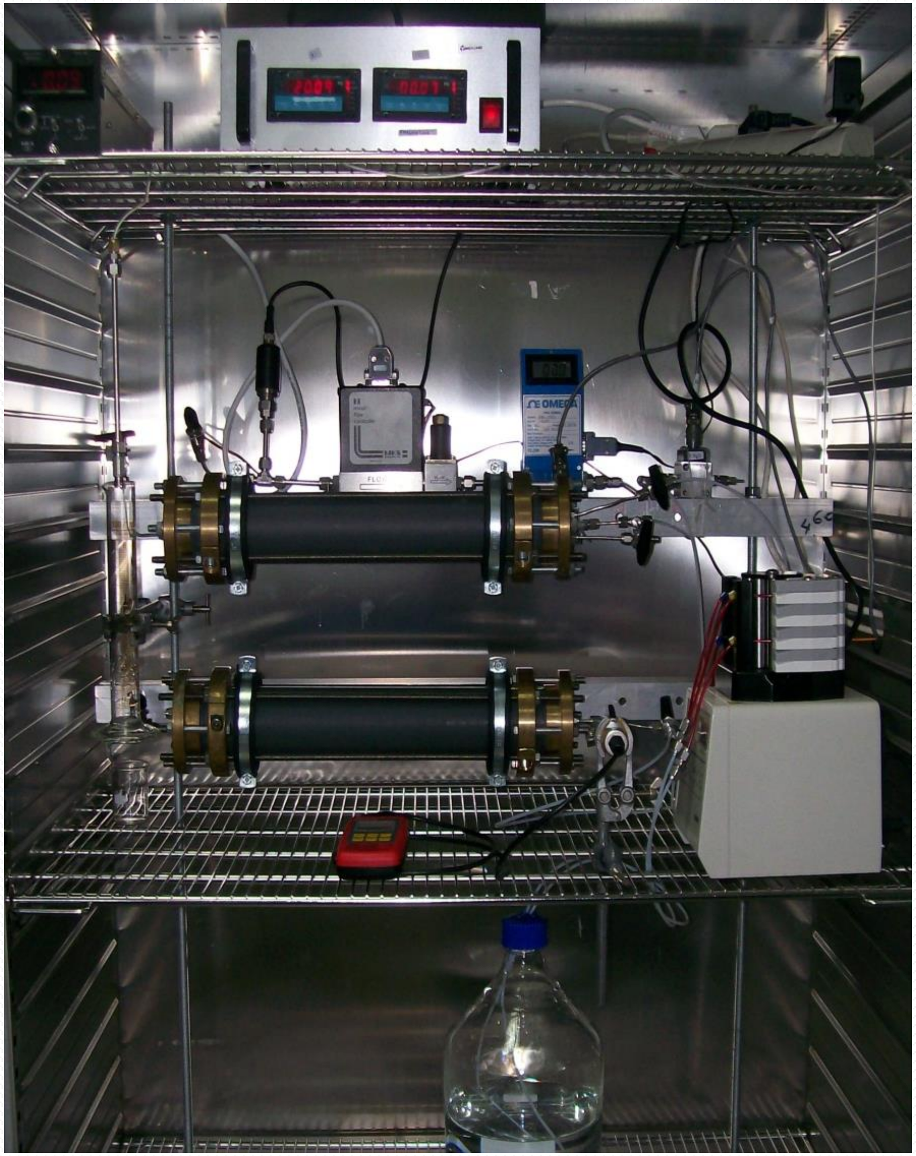
Experimental Setup



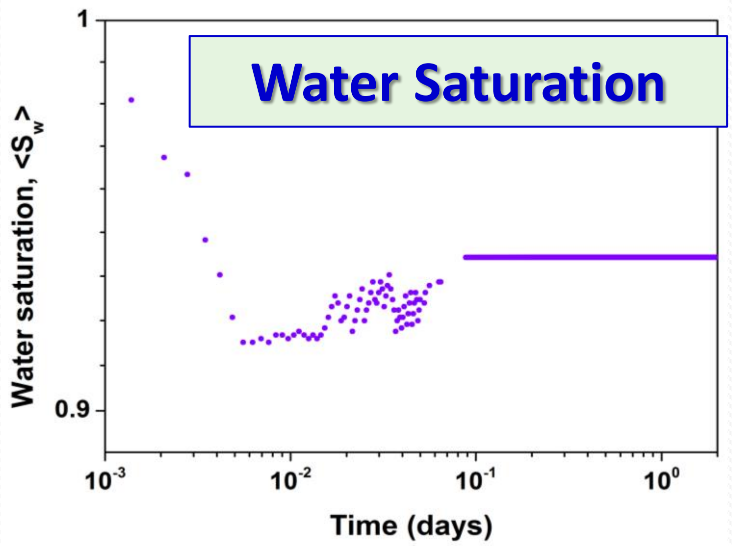
Process Monitoring

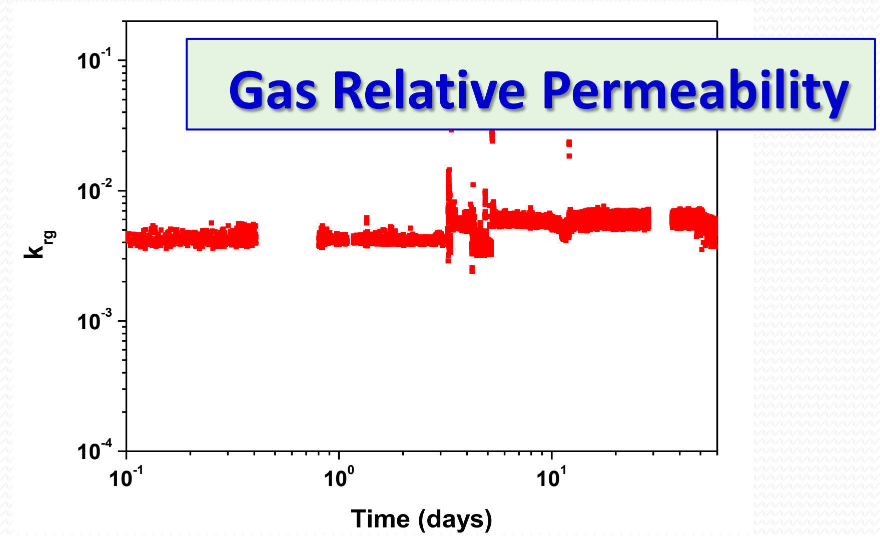
Measured Variables

1. Pressure drop of H_2O and CO_2 across columns
2. Water saturation in CO_2 column
3. pH & electrical conductivity in water effluents
4. Concentrations of metal cations in water effluents
5. Metal content in sand before and after experiment

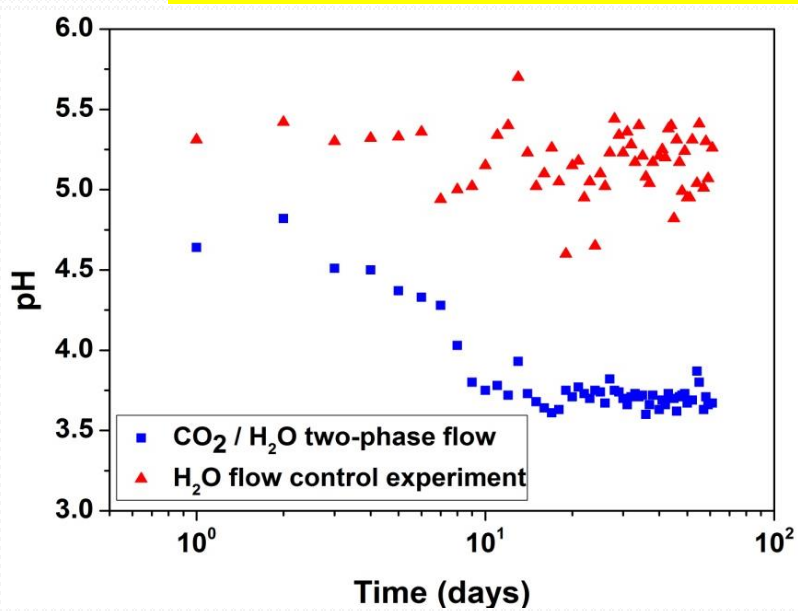


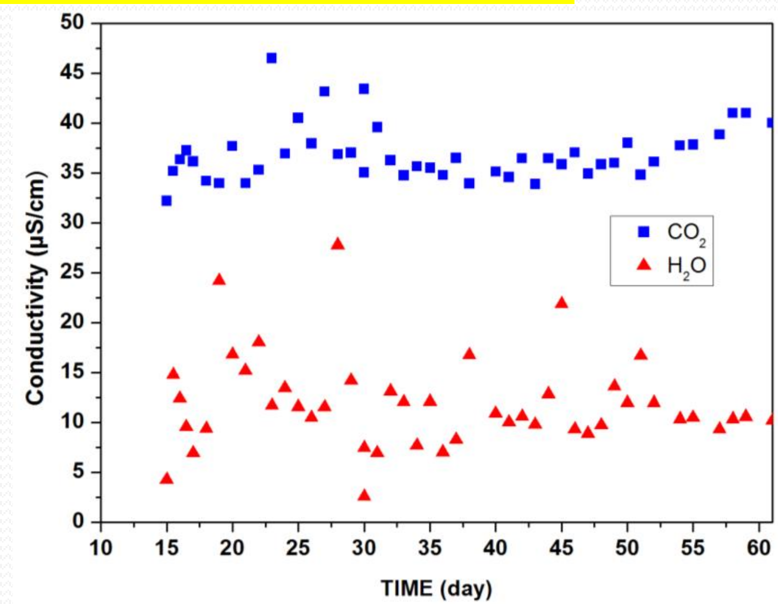
Saturation and Gas Relative Permeability Effluent pH and Electrical Conductivity





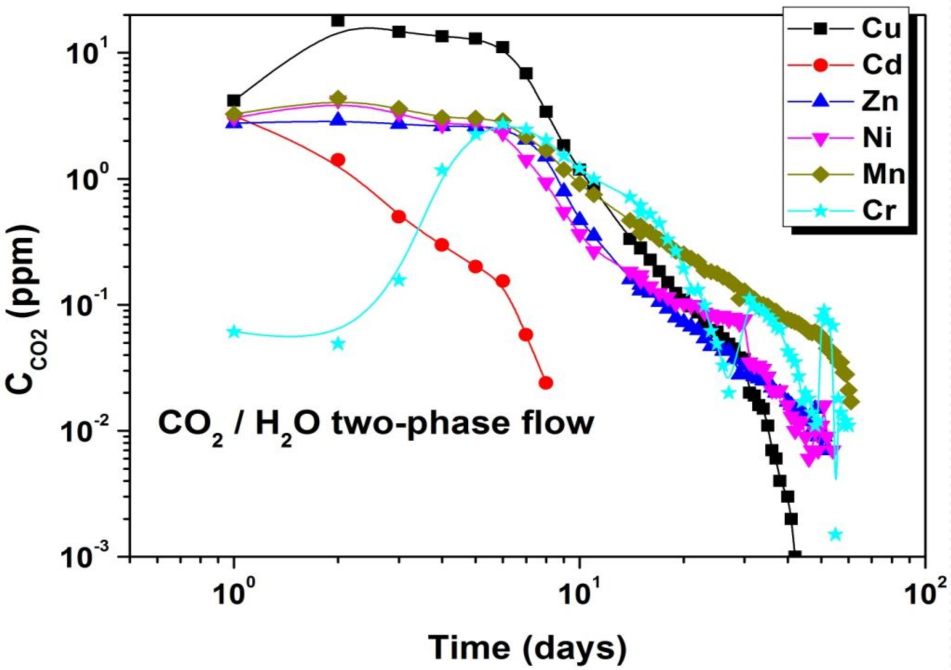
End (steady-state) gas permeability: $k_{rg}^{0}(S_w = 0.93) = 0.005$

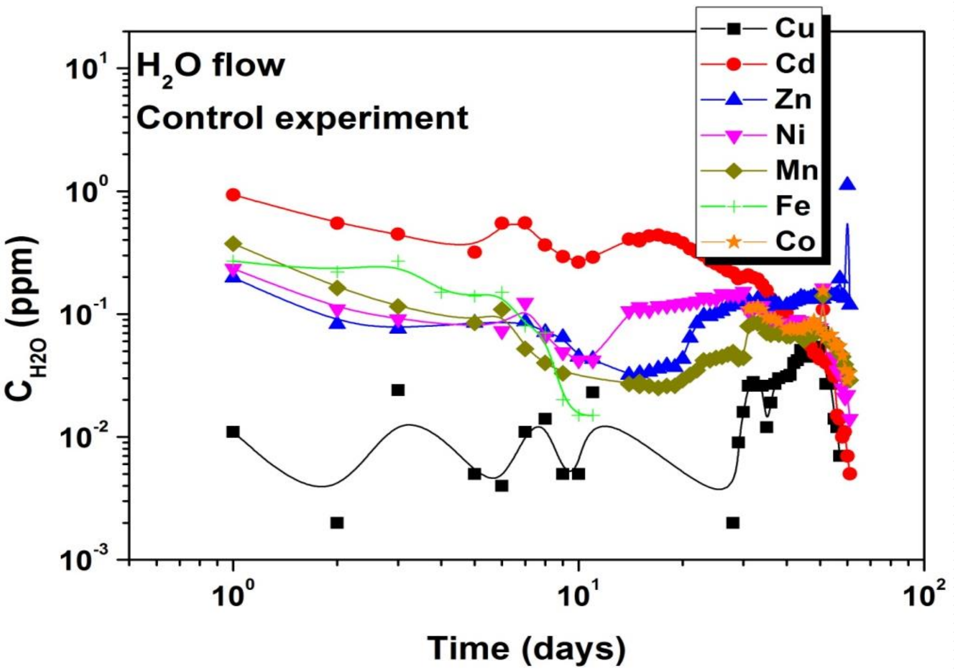




Dissolved Metal Concentration

Transient variation of cation concentration in column effluent with Atomic Absorption Spectroscopy (AAS)



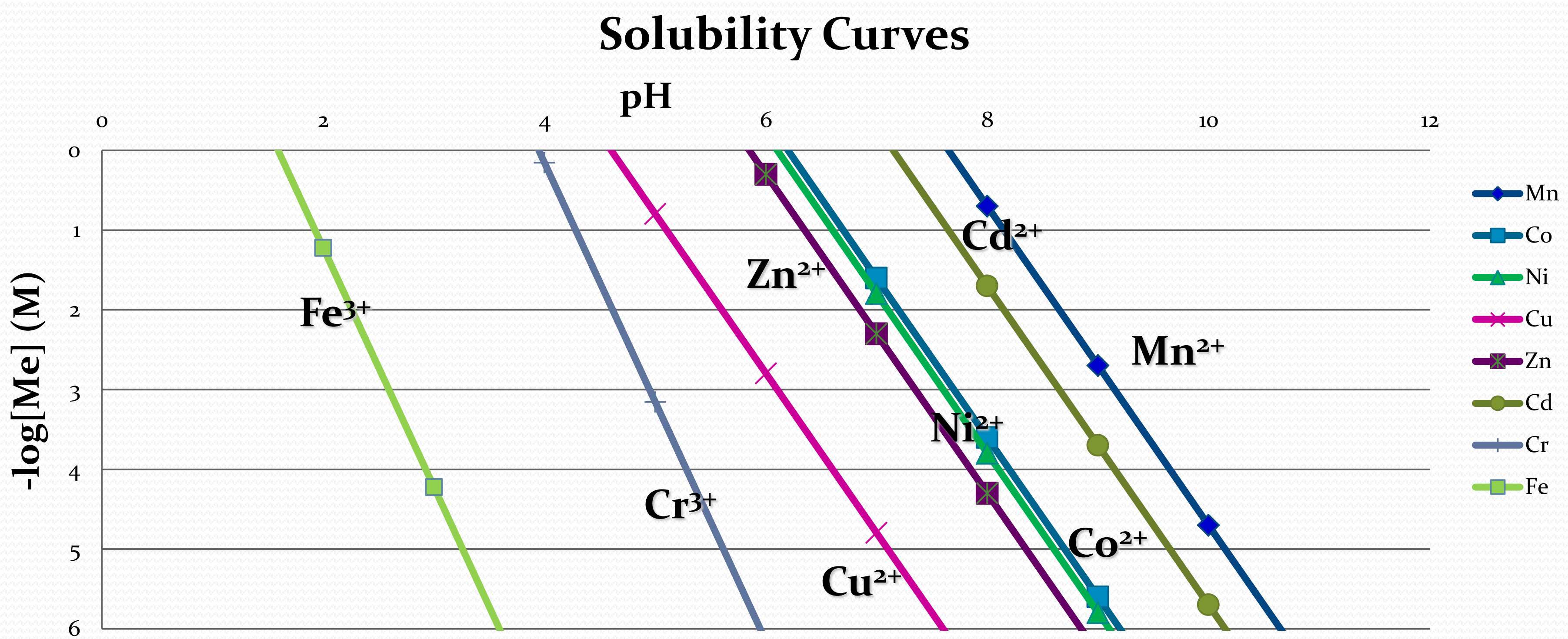


CO_2 Column

H_2O Column

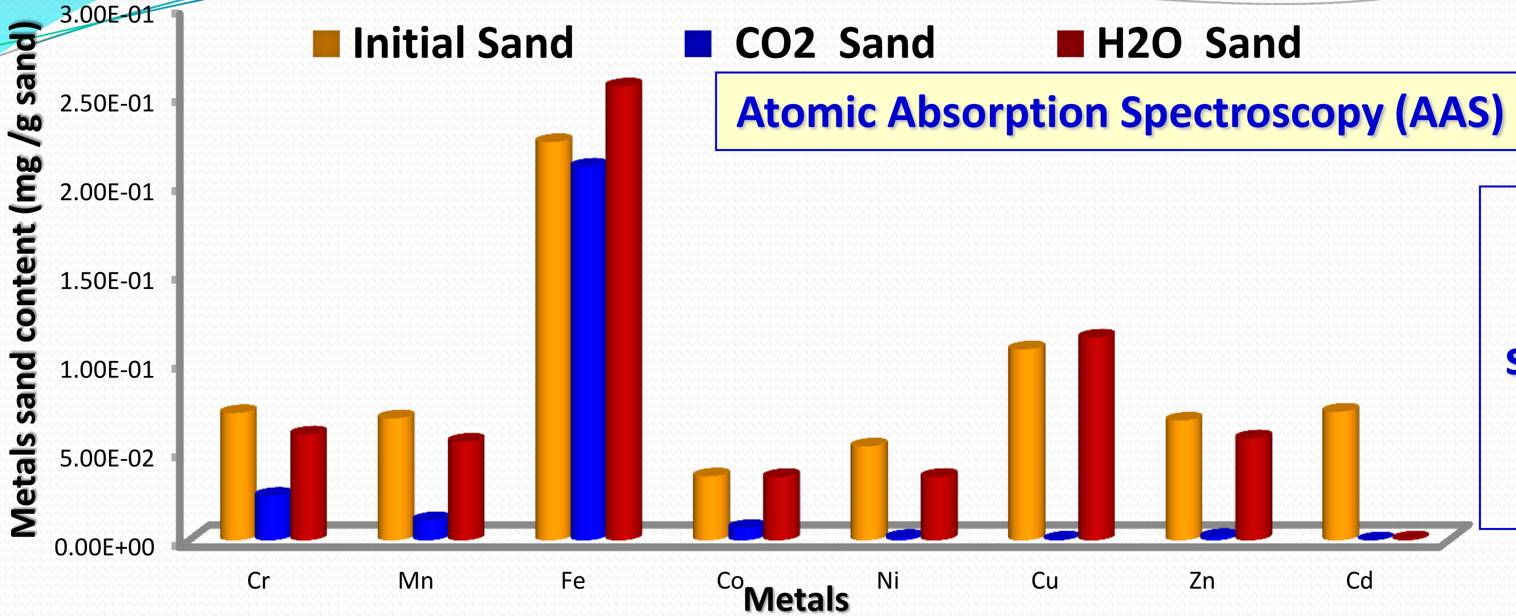
Metal Solubility Curves

Equilibrium cconcentration of metals dissolved from solid oxides /hydroxides as function of pH



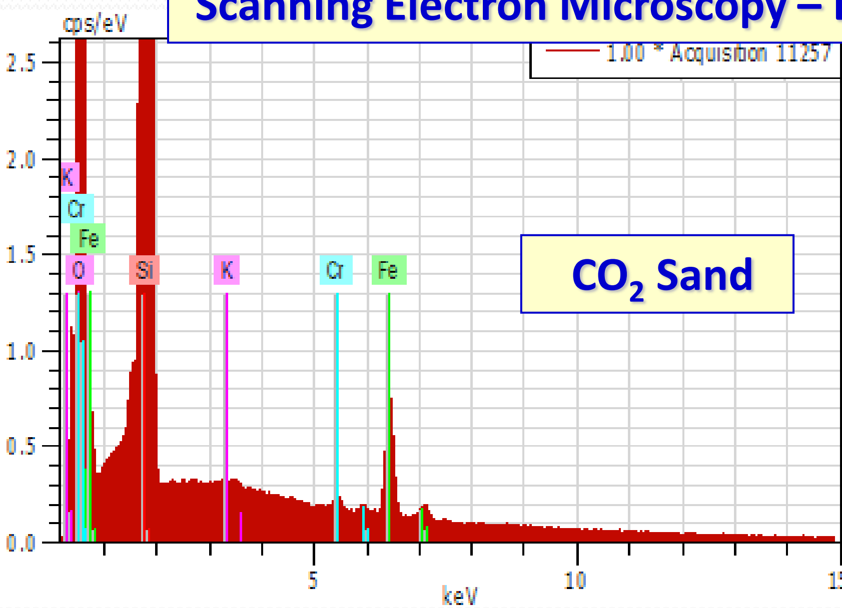
Bradl, «Heavy Metals in the Environment», Elsevier (2005)

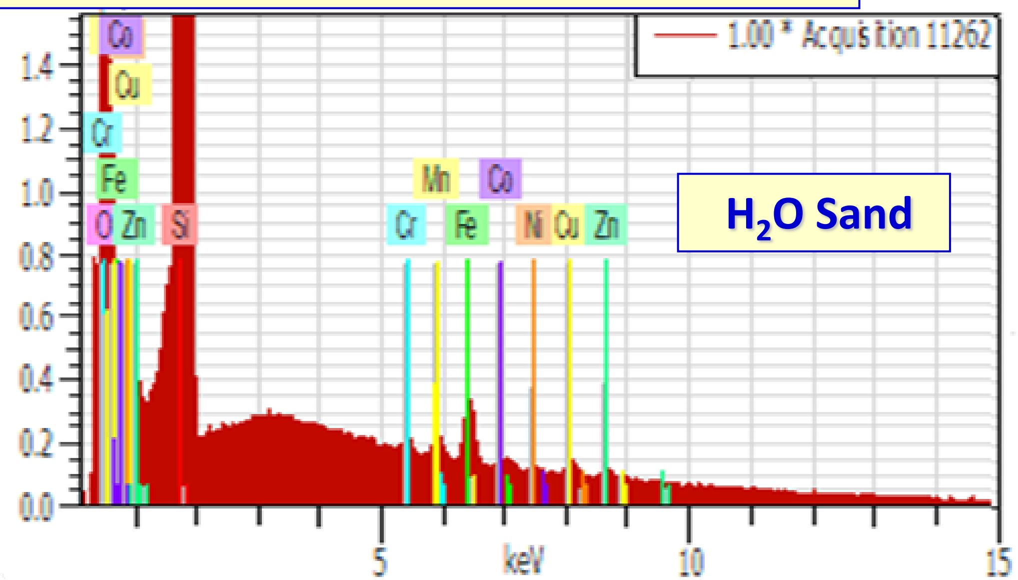
Residual Metals in Sand by AAS and SEM-EDS



Content of metals in the sand before and after the flow experiments

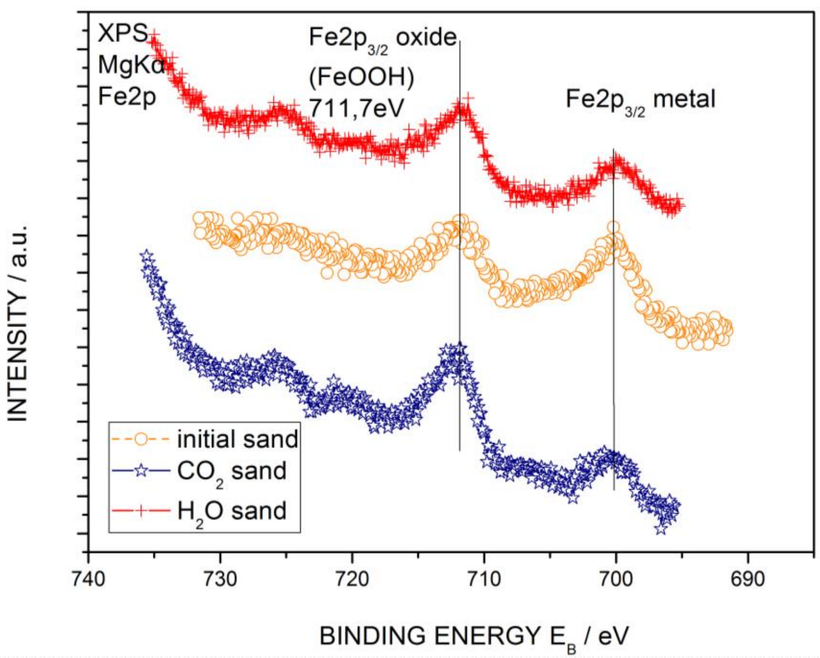
Scanning Electron Microscopy – Energy Dispersion Spectroscopy (SEM – EDS)

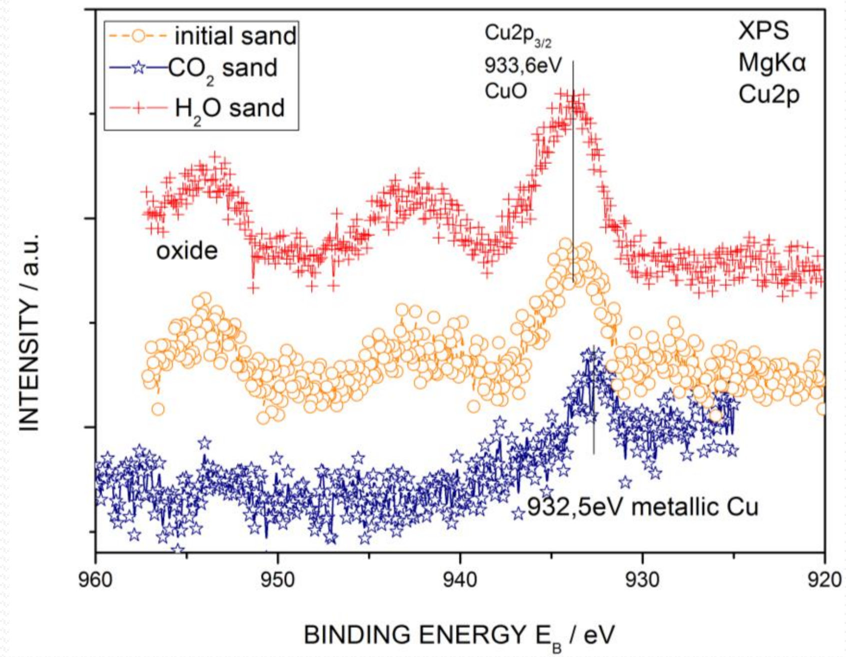




Metal Species on Solid Surface (XPS)

X-ray photoelectron spectroscopy





Species	Cr_2O_3	$Cr(OH)_3$	Cr	MnO_2	FeOOH	Fe	Co	NiO	Ni_2O_3	CuO	Cu	ZnO	Zn	$Cd(OH)_2$
Initial	++	-	++	++	++	++	-	+	-	++	-	++	++	++
H_2O Sand	-	++	-	++	++	++	T	-	+	+	-	+	+	+
CO_2 Sand	+	-	+	T	++	++	-	-	-	-	+ +	-	T	-

++ =strong presence, + =weak presence, - =absence, T =traces

Equilibrium Batch Experiments

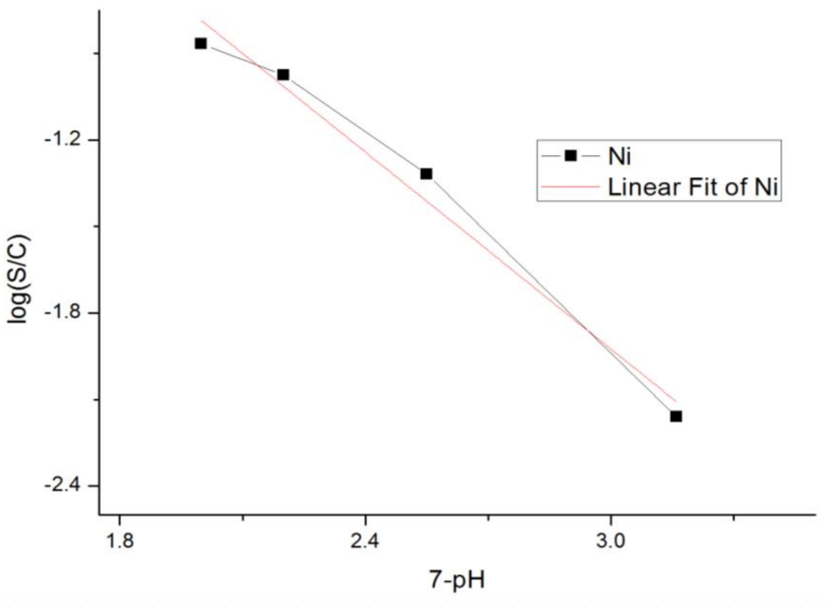
Batch experiments were conducted in different pH ranges (3.8 to 5) with the help of acetic acid in order to define K_d

$$S = K_d C$$

$$\log K_d = \log K_{d0} - m(7 - pH)$$

S → concentrations of the metals on the solid phase after desorption
C → concentrations of the metals in the aqueous phase
K_d → partition coefficient

Metals	K_{d0}	m
Cr	3.3417	1.3963
Mn	1.1868	1.0796
Fe	0.4348	0.2575
Co	-0.5042	0.448
Ni	1.4945	1.1401
Cu	5.8867	2.5633
Zn	3.0484	1.7103
Cd	-0.1569	0.8079



Mathematical Model

Estimated Parameters

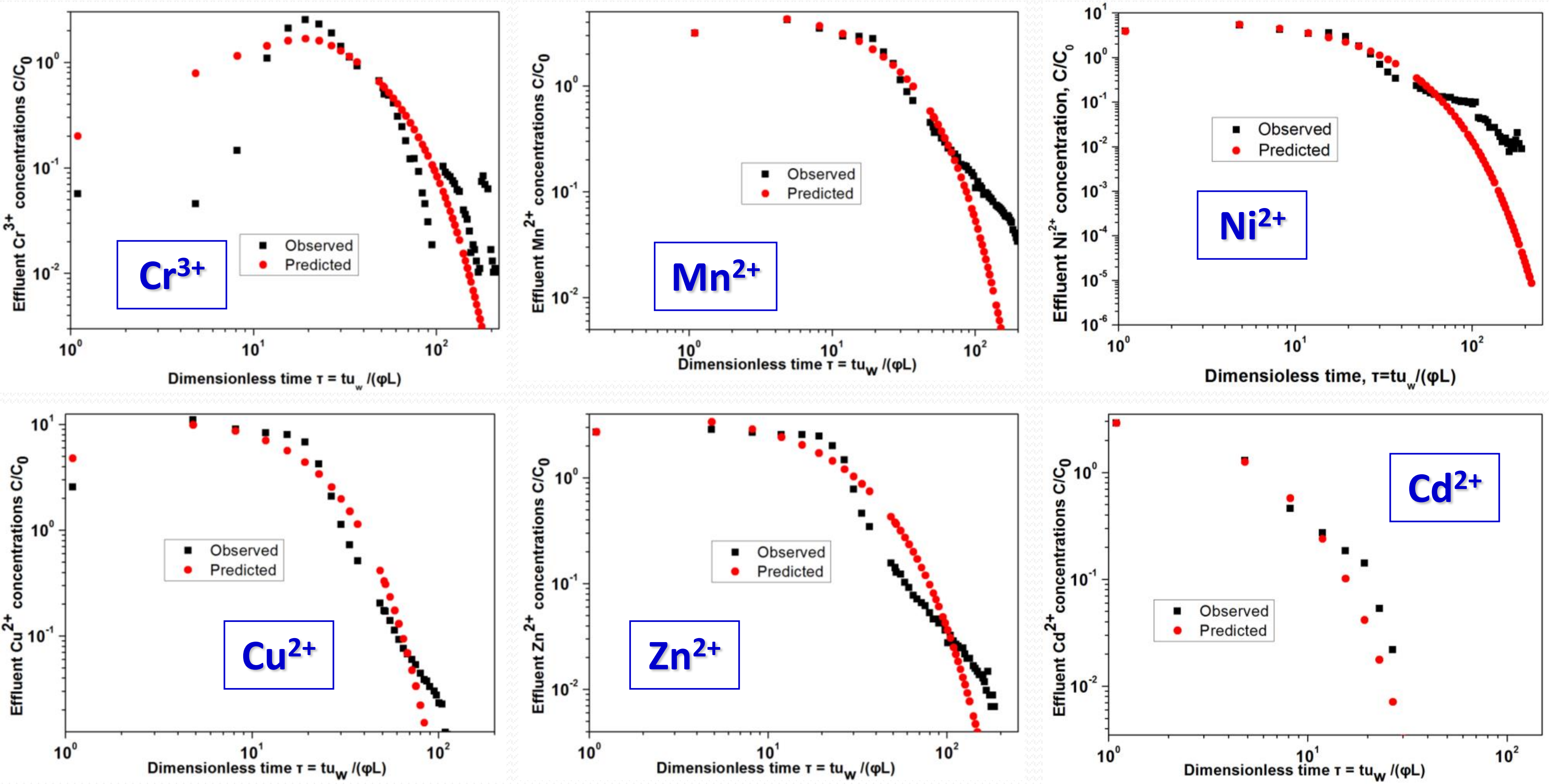
a → desorption rate coefficient
f → fraction of equilibrium of sites
K_{d0} → partition coefficient
m → parameter m (constant)

ASSUMPTIONS

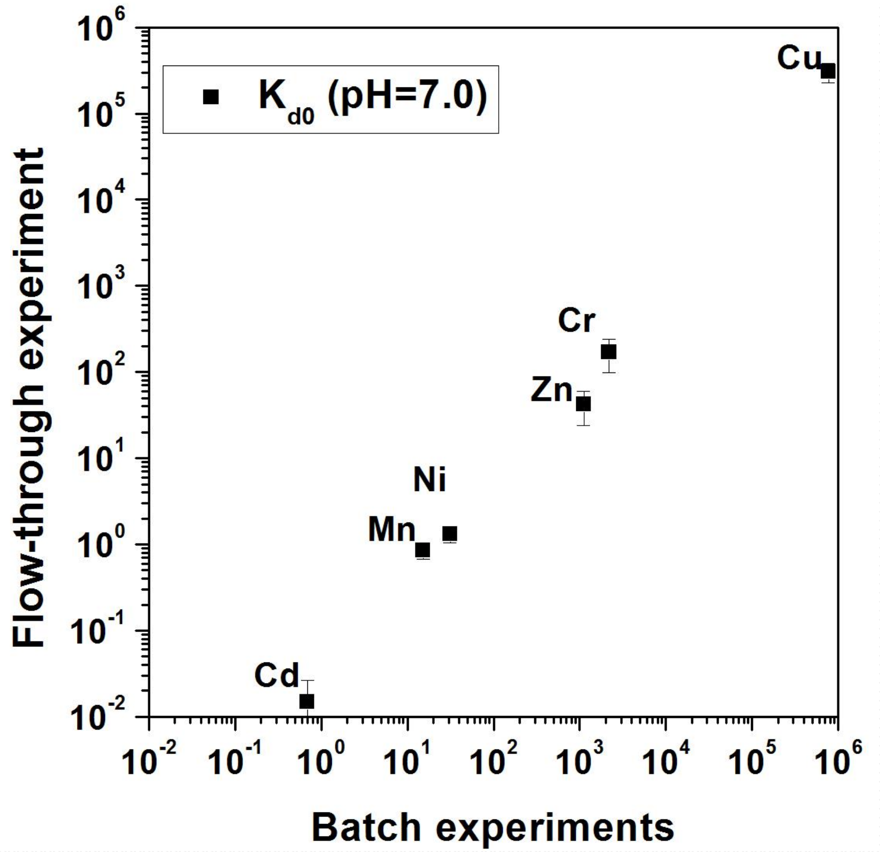
1) 1 – Dimensional flow
2) The parameters for each metal are estimated individually
3) Water saturation and water/gas relative permeability remain constant
4) Dissolved CO_2 is at chemical equilibrium
5) Homogeneous distribution of the elements through the whole sand
6) Two-site adsorption-desorption model to describe metal mobilization

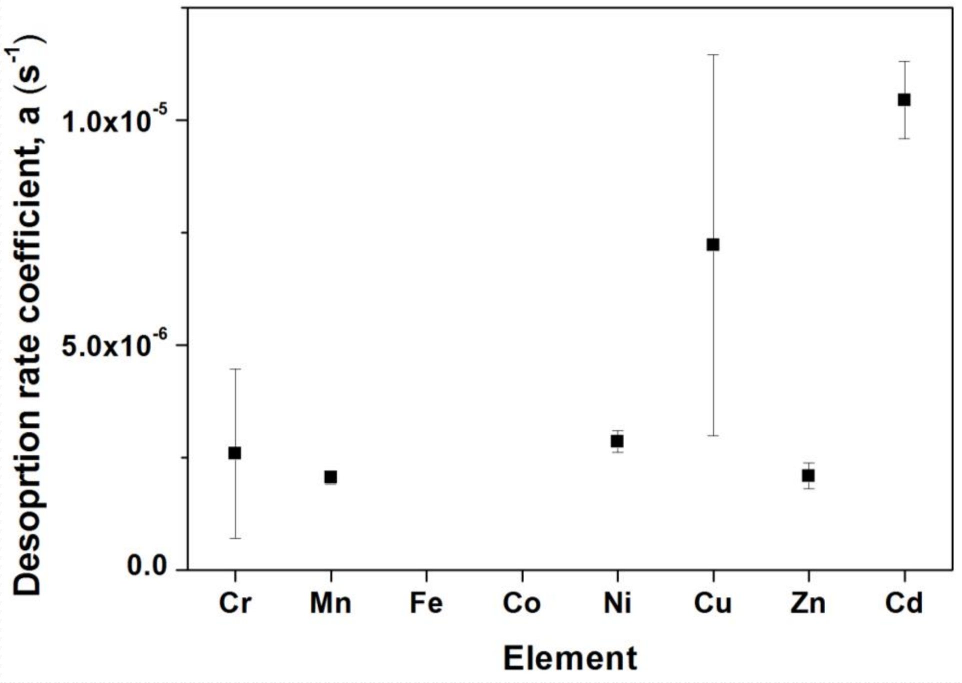
Results of Numerical Modeling

Predicted versus observed responses of metal concentration in effluent



Estimated Parameters





↓ K_{d0} → the metal is desorbed much more easily

↑ a → the metal is desorbed much faster

Conclusions

- A flow-through experiment of the simultaneous two-phase flow of gas CO_2 and water was performed in a sand column of controlled mineralogy
- The chemical analysis of effluents was done by AAS
- The chemical characterization of sand was done by SEM-EDS and XPS
- Supplementary batch experiments were conducted to find the dependence of the partition coefficient on the pH

- pH reduction causes the selective mobilization of various metals according to the sensitivity of their solubility to pH
- Due to CO_2 dissolution, the concentration of metals in aqueous phase may increase by one order of magnitude
- A dynamic mathematical model (PDEs) was developed to describe metal release and dispersion in soil column
- The parameters estimated with inverse modeling are indicative of metal mobilization

Thank you for your attention

Acknowledgements

This research has been co-financed by the European Union (European Social Fund – ESF) and Greek National Funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: Thales, investing in knowledge society through the European Social Fund

European Union
European Social Fund

OPERATIONAL PROGRAMME
EDUCATION AND LIFELONG LEARNING
investing in knowledge society
MINISTRY OF EDUCATION, LIFELONG LEARNING AND RELIGIOUS AFFAIRS
MANAGING AUTHORITY

NSRF
2007-2013
programme for development
EUROPEAN SOCIAL FUND

Co- financed by Greece and the European Union

Dr. L. Sygenlou is acknowledged for XPS analysis, and Dr. V. Dracopoulos for SEM-EDS analysis