BELBaR Project

TESTING OF SORPTION AND DESORPTION BEHAVIOR OF RADIONUCLIDES IN COLUMN WITH CRUSHED GRANITE: DETERMINATION OF SYSTEM BEHAVIOR WITHOUT PRESENCE OF COLLOIDS

WP3

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Presentation outline

- **Goals of experiments**
- **Column experiments**
  - Solid phase
  - Liquid phase
  - Tracers
  - Evaluation
- **Results**
- **Conclusion**

Goals of experiments

- Study of sorption and desorption behavior of chosen radionuclides using **column experiments**
- Information about radionuclide transport through crushed granite
- Reference study: comparison of differerent tracer behavior without colloid presence

- The planned experiments will study migration of radionuclides through crushed granite material in presence of colloids

Column experiments

- Study of sorption and desorption processes

- Determination of transport parameters

Setup for column experiments

- **Plastic columns**
  - 1.3 cm inner diameter
  - 5.4 cm bed height
  - 6.4 cm^3 bed volume
- **4-double head peristaltic pump**
- **8-outlet manifold**
- **Reservoir of liquid phase**

Solid phase

- Granitic rock from Melechov massive, Central Bohemian Massive, Czech Republic
- 97.5 – 98.7 m depth
- Two types of crystalline rocks
  - pure granite (PDM 1-1)
  - fracture filling materials (PDM 1-2)
- Majority minerals: quartz, feldspar
- Minority minerals: mica, chlorite
- Four grain size fractions

Solid phase

- Composition of used crystalline rock

Minerals	Content (wt.%)							
	a < 0.063 mm		b 0.125 – 0.063 mm		c 0.63 – 0.125 mm		d 0.8 – 0.63 mm	
	PDM 1-1	PDM 1-2	PDM 1-1	PDM 1-2	PDM 1-1	PDM 1-2	PDM 1-1	PDM 1-2
quartz	27	24	30	33	32	37	31	33
orthoclase	37	24	32	23	31	23	31	27
plagioclase	23	27	20	27	18	24	24	25
mica	8	7	12	5	14	7	10	5
chlorite	5	18	6	12	5	9	4	10

Liquid phase

- Synthetic granitic water (depth 100 m)

Ions	concentration (mg/L)
pH	8.03
Na^{+}	10.6
K^{+}	1.8
Ca^{2+}	27.0
Mg^{2+}	6.4
Cl^{-}	42.4
SO_4^{2-}	27.7
NO_3^{-}	6.3
HCO_3^{2-}	30.4
F^{-}	0.2

Tracers

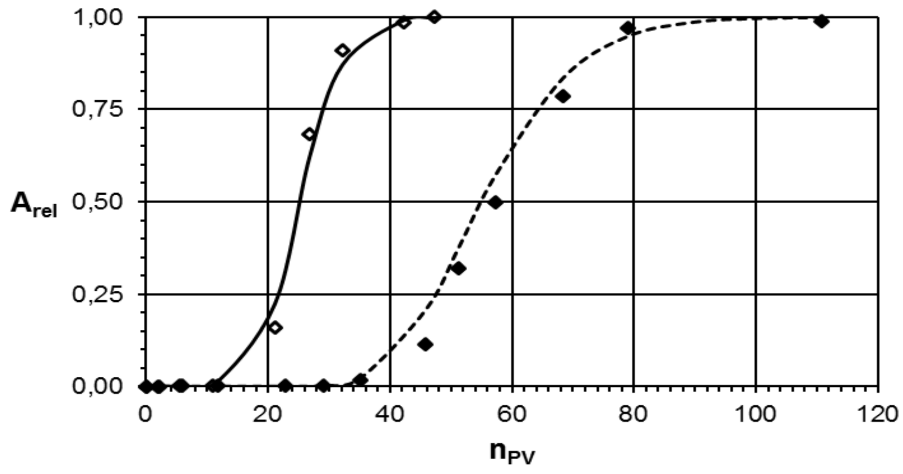
Tracer	Half live	Specie	Measurement
^{3}H	12.4 years	HTO	Automatic Liquid Scintillation Counter HIDEX
^{36}Cl	301 000 years	Cl^{-}	
^{85}Sr	64.8 days	Sr^{2+}	Automatic gama counter WIZARD
Se(IV)	stable	SeO_3^{2-}	ICP-MS
Se(VI)	stable	SeO_4^{2-}	

Evaluation of experiments

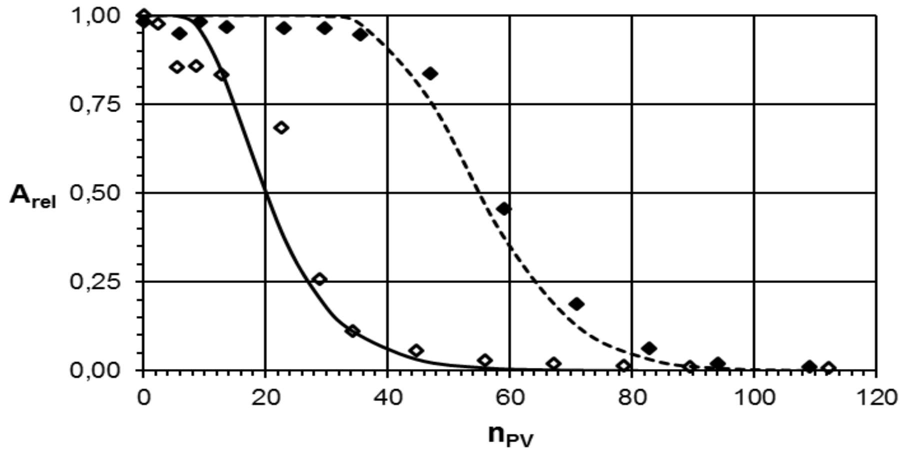
- **Experimental sorption and desorption breakthrough curves (BTC)**
  - evalution of retardation coefficient (R)
- **BTC fitted using non-linear regression**
  - evalution of other transport parameters

Breakthrough curves

- Sorption BTC
  - S-shape
  - retardation coefficient R_{expS}
  - X axis – number of pore volumes n_{PV}
  - Y axis – relative activity (concentration)



- Desorption BTC
  - Ƨ-shape
  - retardartion coefficient R_{expD}



Theoretical evaluation of experimental data

- Fitting of experimental data by complementary error function (erfc)
- Erfc-type equation
  - assumption of non-linear regression
  - result of the analytical solution of 1-D advection-dispersion equation
- Evalution of transport parametres
  - retardation coefficients (R_{teorS}, R_{teorD})
  - distribution coefficients (K_{dteorS}, K_{dteorD})
  - Peclet number (Pe)
  - dispersion coefficient (D_d)
- WSOS/DF
  - fitting criterion (the goodness-of-fit), acceptable if $0.1 \leq WSOS/DF \geq 20$

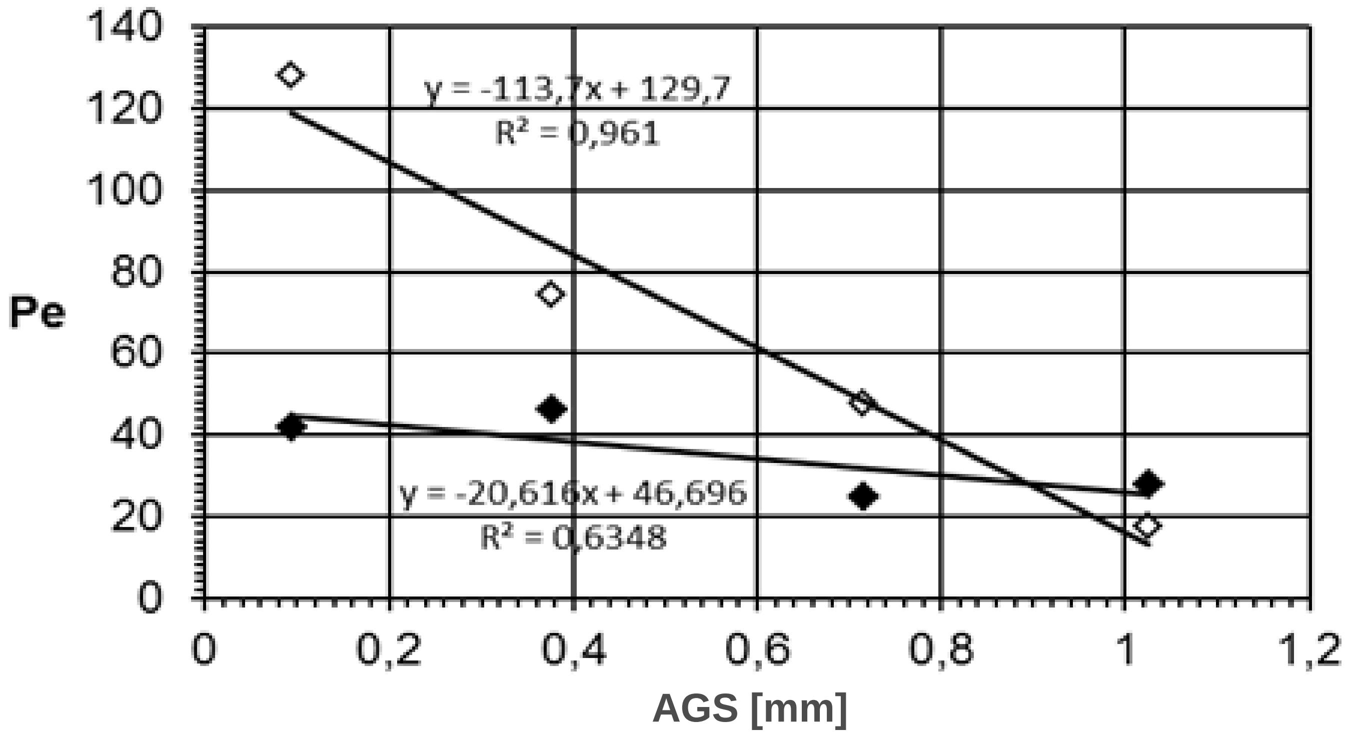
RESULTS

^{3}H – transport parameters

- **R_{exp}, R_{theor} → 1**
- **K_{dteor} → 0**
  - conservative tracer
  - no influence of granitic grain size on retardation coefficients
  - suitable for determination of granite hydrodynamic parameters
- **Pe – influence of grain size**

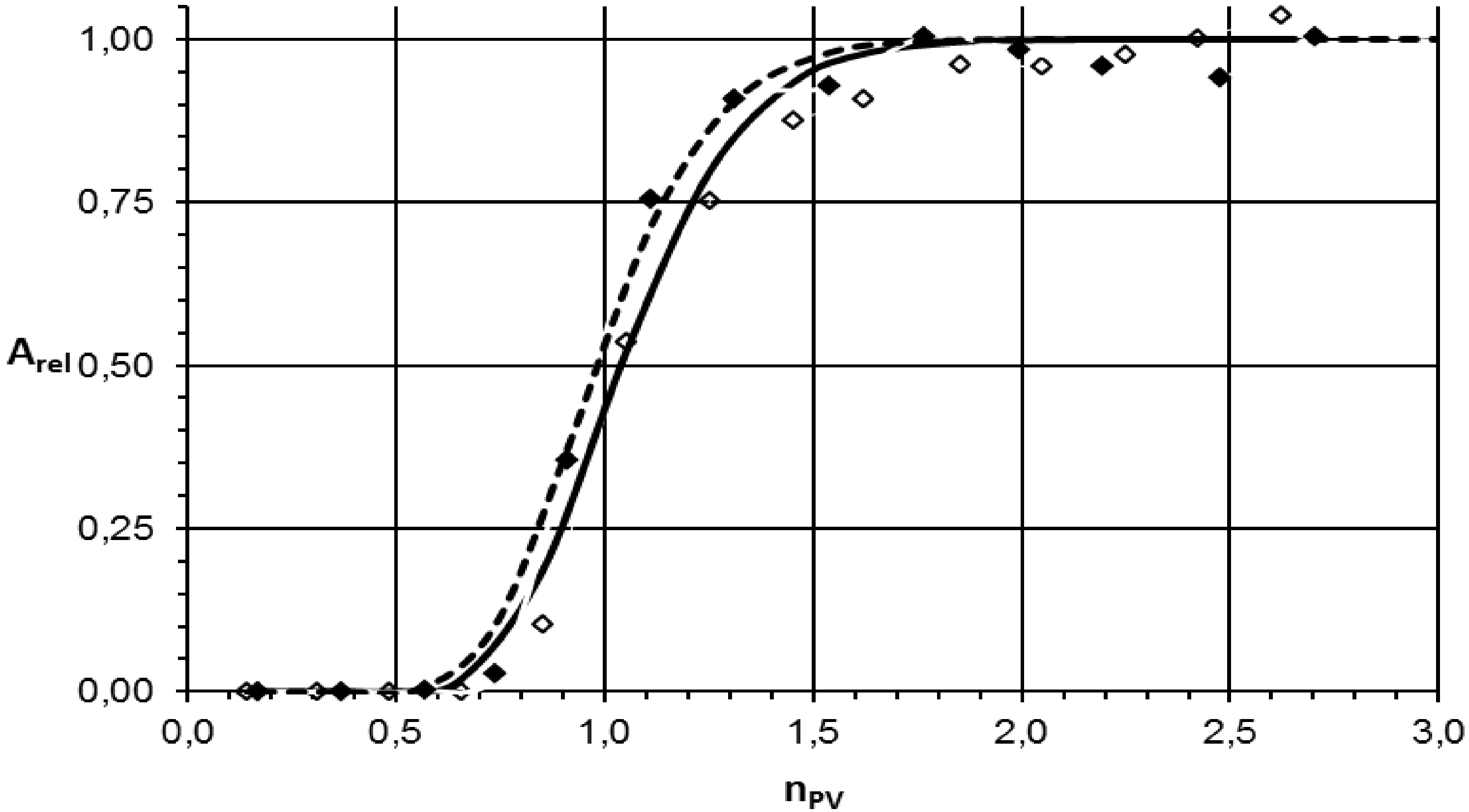
^3H – transport parameters

- Pe decreases with increasing grain size of granite
  (more significantly than for fracture filling materials)



Dependence of Pe on average grain size (AGS) of pure granite (blank symbols) and fracture infill material (filled symbols)

^3H – sorption BTC



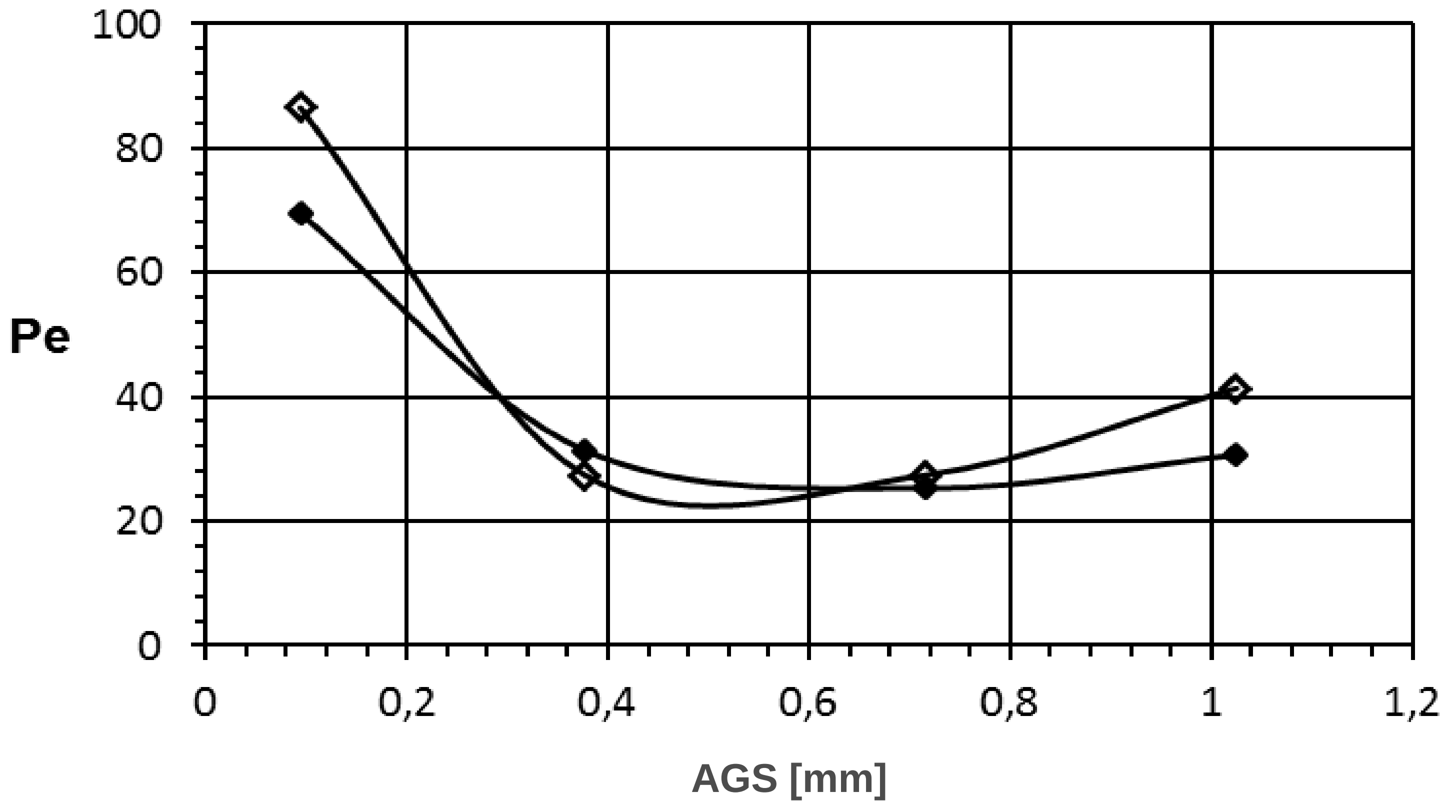
Ilustrative sorption BTC of ^3H in granite (blank symbols) and in fracture infill (filled symbols) of 0.125 – 0.063 mm grain size (symbols – experimental values, curves – calculated values, solid lines to blank symbols, dotted lines to filled symbols)

^{36}Cl – transport parameters

- **$R_{teorS} > 1$**
  - possible anionic exclusion
  - no influence of granitic grain size on retardation coefficients
- **$R_{expS} \rightarrow 1$, $K_{dteor} \rightarrow 0$**
  - non-sorbing tracer
  - no influence of granitic grain size on retardation coefficients
- **Pe – influence of granitic grain size**

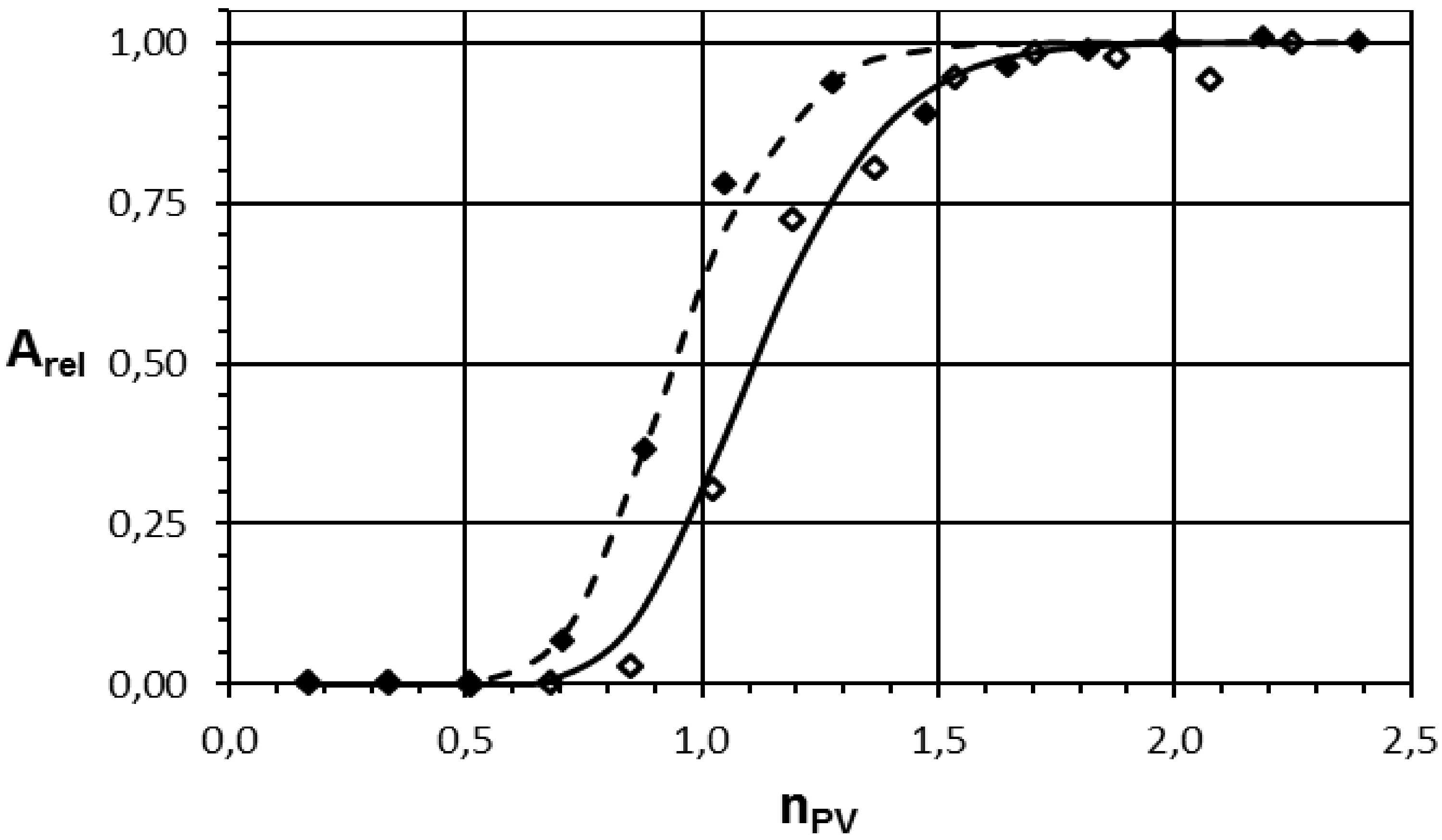
^{36}Cl – transport parameters

- no significant difference between granite and fracture infill
- the highest value of Pe for fraction a (< 0.063 mm)



Dependence of Pe on average grain size (AGS) of pure granite (blank symbols) and fracture infill material (filled symbols)

^{36}Cl – sorption BTC

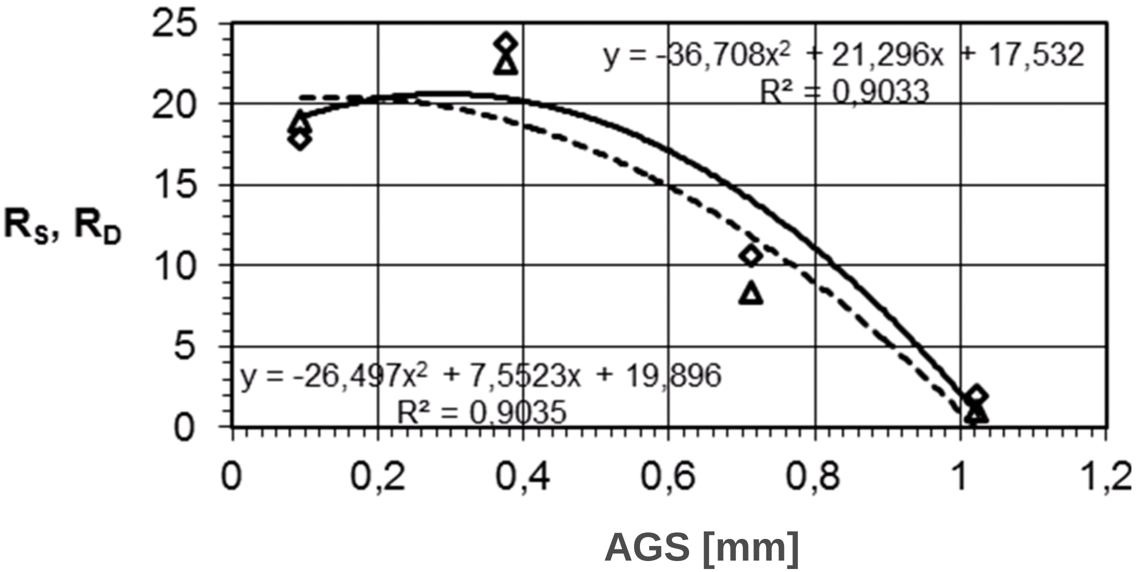


llustrative sorption BTC of ^{36}Cl in granite (blank symbols) and in fracture infill (filled symbols) of 0.125 – 0.063 mm grain size (symbols – experimental values, curves – calculated values, solid lines to blank symbols, dotted lines to filled symbols)

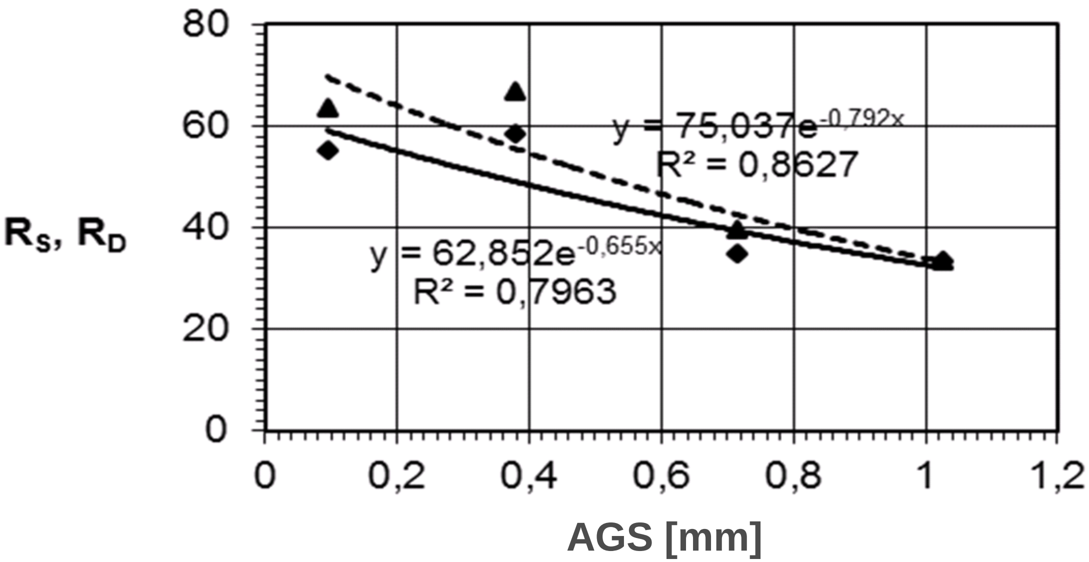
^{85}Sr – transport parameters

- **R, K_d (granite) < R, K_d (infill)**
  - sorption of ^{85}Sr in fracture infill (filled symbols) is 2.5-times higher than in granite (blank symbols) in case of all granitic fractions
  - sorption ( ) and desorption (Δ) decrease with increasing grain size → decrease of sorption capacity of crystalline rock

- Granite

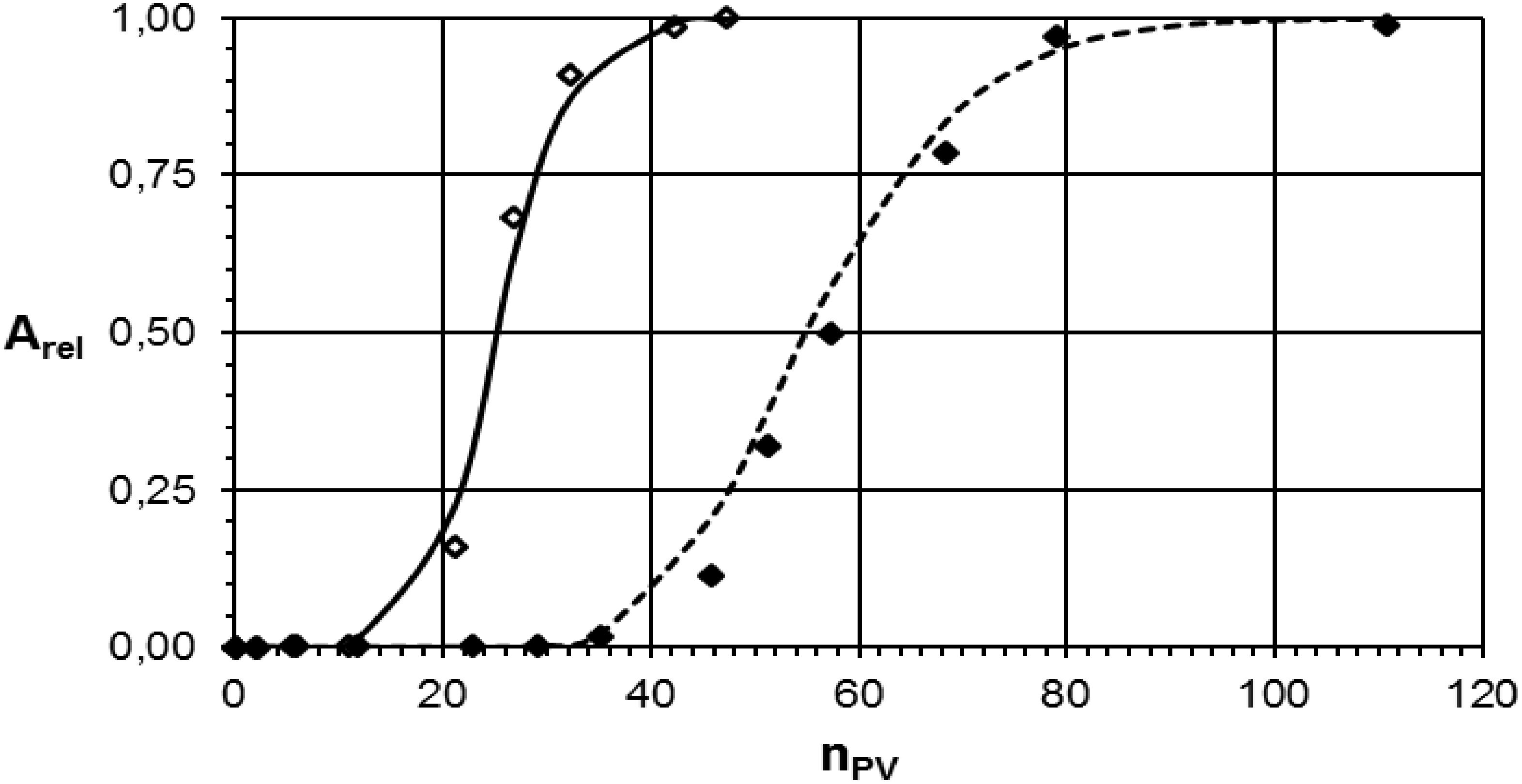


- Fracture infill material



Dependence of R_S ( ) and R_D (Δ) on average grain size (AGS) of pure granite (blank symbols) and fracture infill material (filled symbols)

^{85}Sr – sorption BTC



llustrative sorption BTC of ^{85}Sr in granite (blank symbols) and in fracture infill (filled symbols) of 0.125 – 0.063 mm grain size (symbols – experimental values, curves – calculated values, solid lines to blank symbols, dotted lines to filled symbols)

Se(IV) – transport parameters

- **Sorption and desorption are evident in both studied materials**

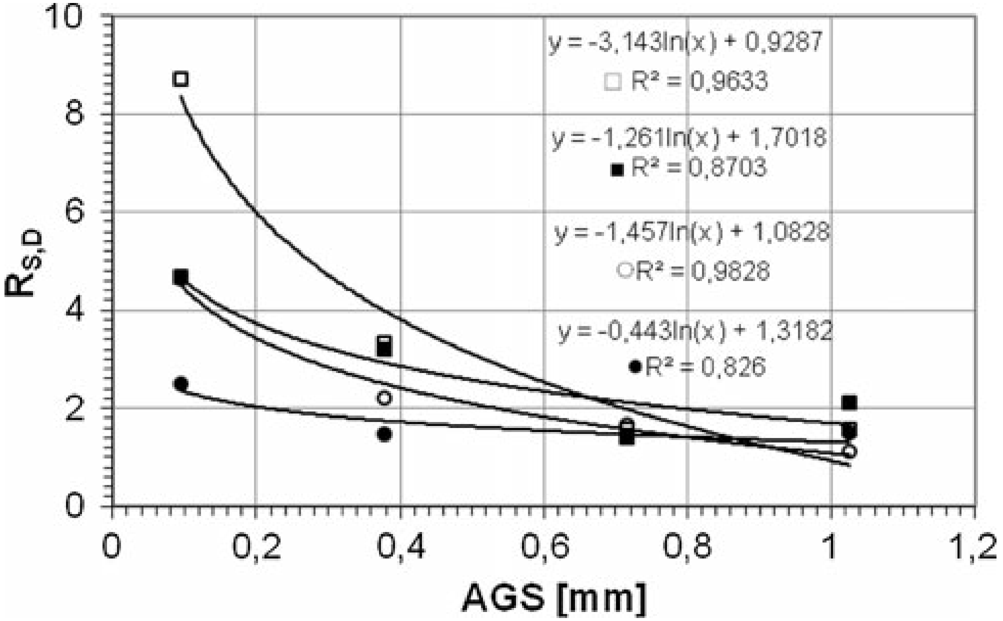
- **Sorption increases with decreasing grain size**

- **K_d, R (granite) < K_d, R (fracture infill)**

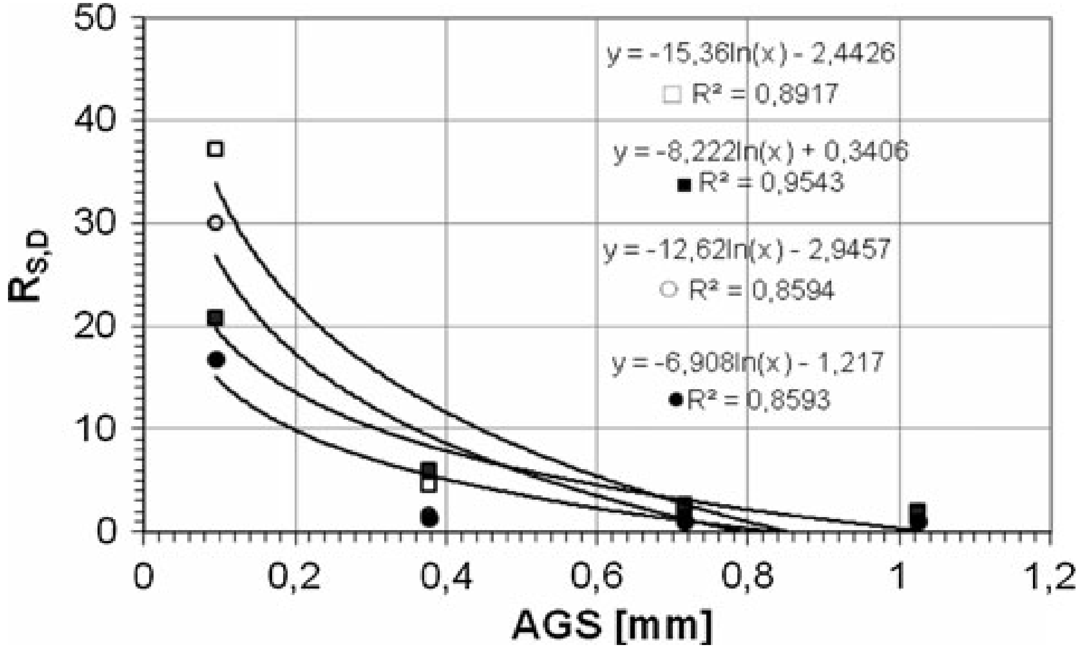
- **K_{dteorS} > K_{dteorD}**
  - certain concentration of selenite takes place on solid phase, especially on fracture infill

Se(IV) – transport parameters

- Granite

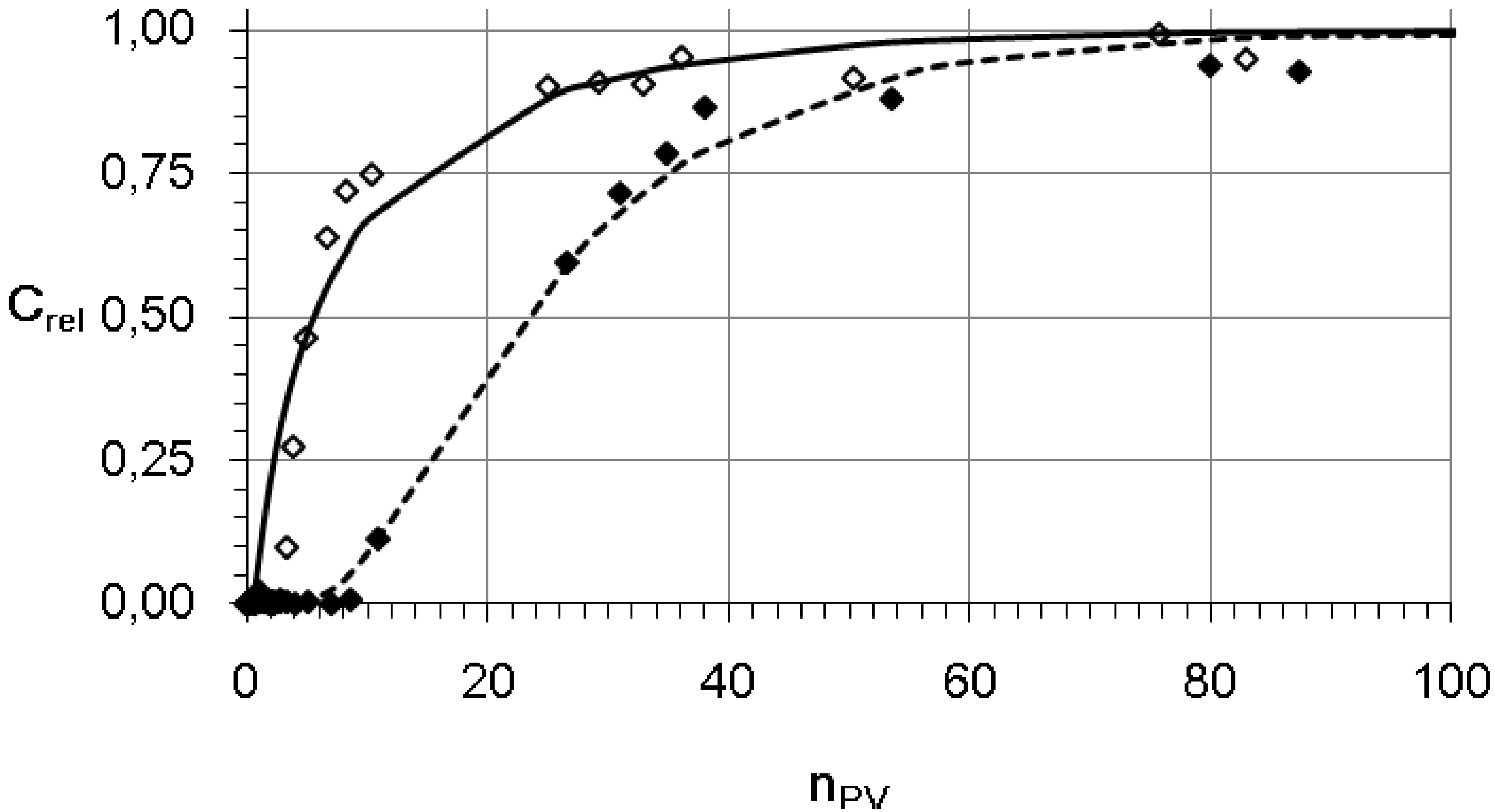


- Fracture infill material



Effect of the average grain size (AGS) on the retardartion coefficients of sorption: R_{expS} (filled square), R_{teorS} (blank square), and desorption: R_{expD} (filled circle), R_{teorD} (blank circle) in granite and fracture infill material

Se(IV) – sorption BTC



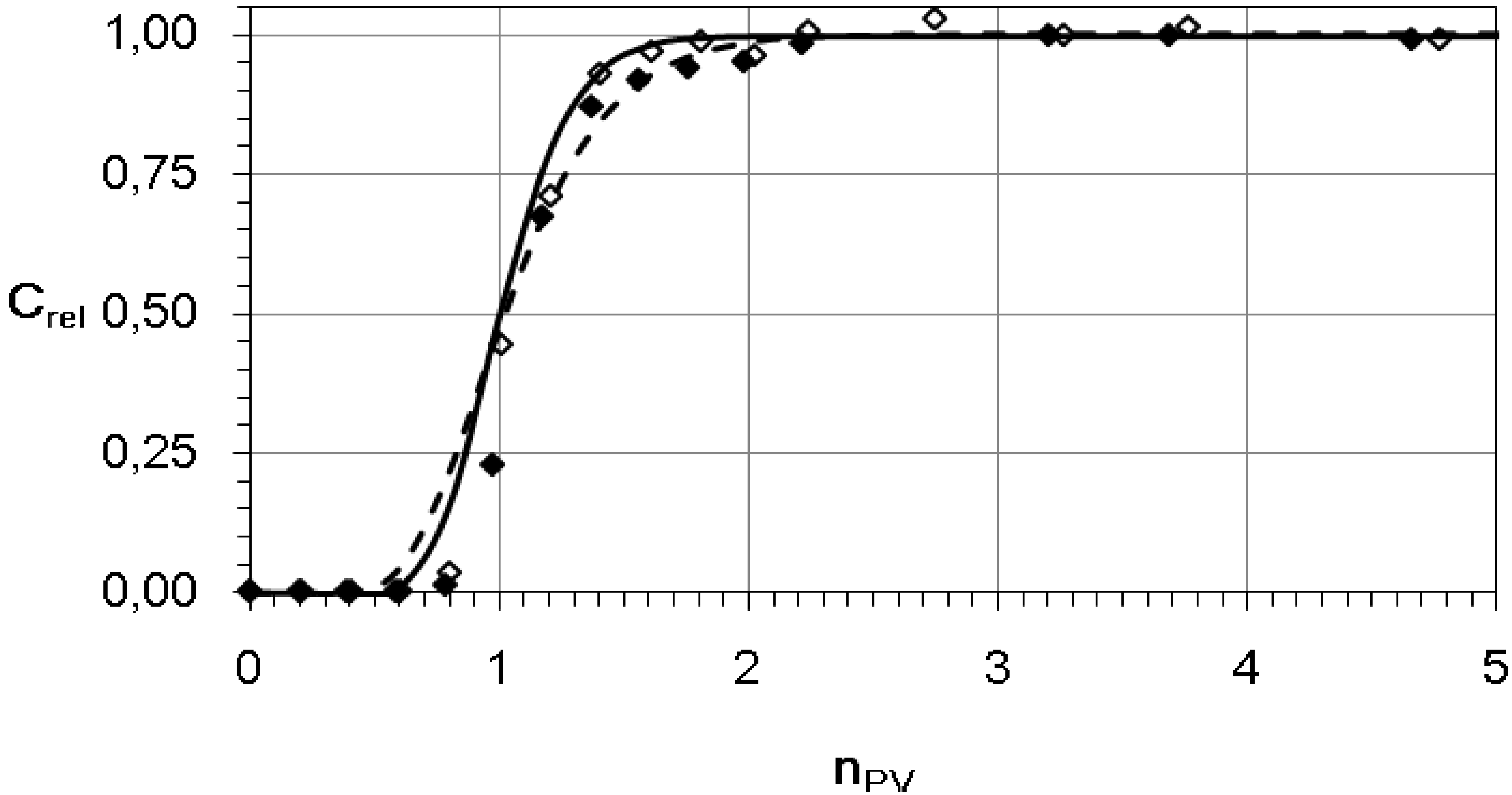
llustrative sorption BTC of Se(IV) in granite (blank symbols) and in fracture infill (filled symbols) of 0.125 – 0.063 mm grain size (symbols – experimental values, curves – calculated values, solid lines to blank symbols, dotted lines to filled symbols)

Se(VI) – transport parameters

- **R_{exp}, R_{theor} → 1**
- **K_{dteor} → 0**
  - conservative tracer
  - no sorption on surface of granite or fracture infill
  - no influence of granitic grain size on retardation coefficients

- **Pe – influence of granitic grain size**
  - no significant difference between granite and fracture infill

Se(VI) – sorption BTC



Ilustrative sorption BTC of Se(VI) in granite (blank symbols) and in fracture infill (filled symbols) of 0.125 – 0.063 mm grain size (symbols – experimental values, curves – calculated values, solid lines to blank symbols, dotted lines to filled symbols)

CONCLUSION

Conclusion

- ^{3}H
  - behavior of conservative tracers without any sorption
  - suitable to determination hydrodynamic parameters of solid phase

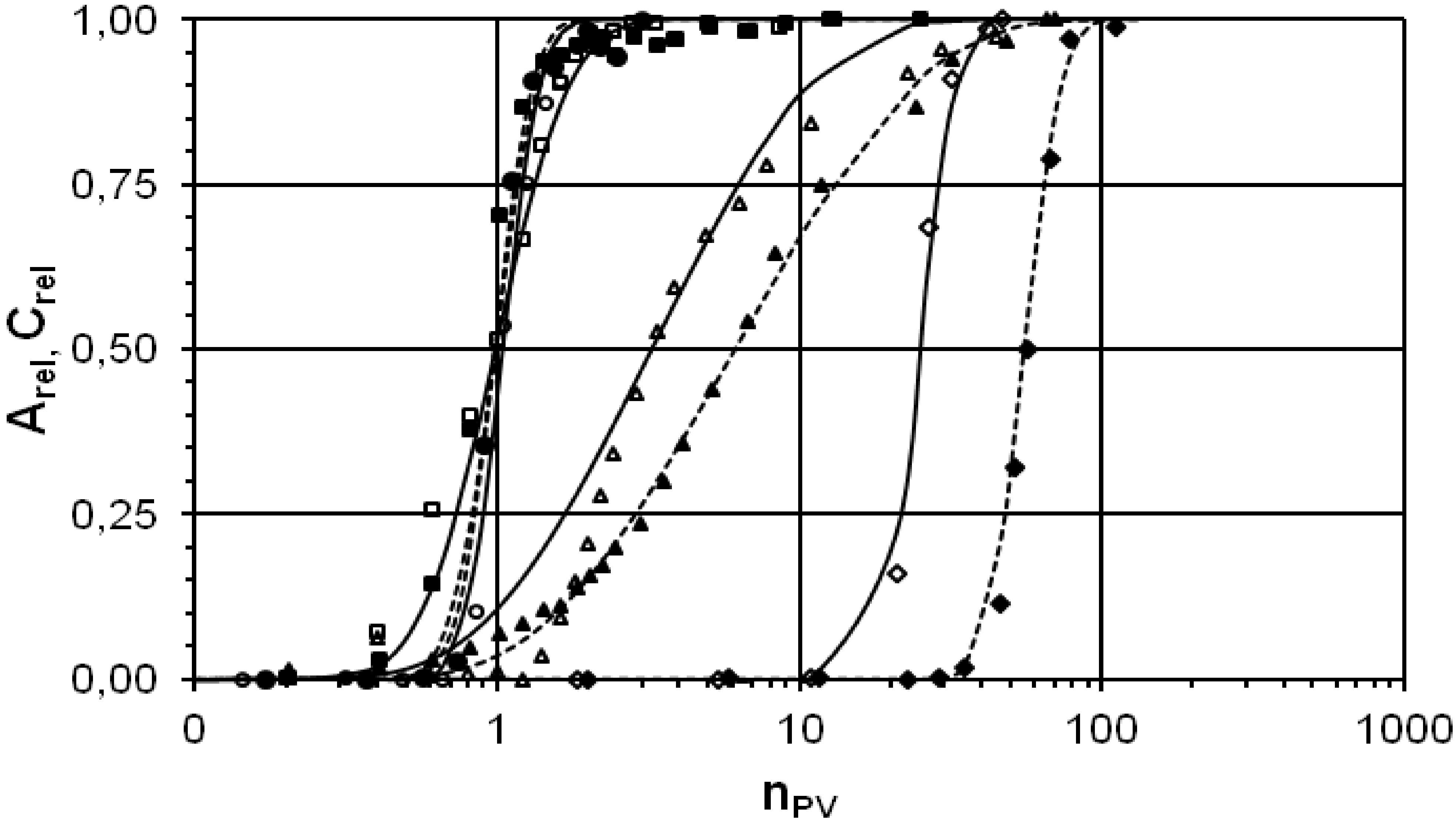
- ^{36}Cl
  - behavior of conservative tracers without any sorption
  - anionic exclusion observed

- ^{85}Sr
  - sorption on granite and fracture infill material
  - higher sorption on fracture infill material
  - values of K_d and R decrease with increasing grain size

Conclusion

- **Se(VI)**
  - behavior of conservative tracers without any sorption
  - similar behavior as ^{3}H and ^{36}Cl

- **Se(IV)**
  - sorption on granite and fracture infill material
  - sorption of Se(IV) in fracture infill is as much as 4.5-times higher than in granite; this difference decreases with increasing grain size
  - influence of granitic size and granite composition
  - sorption increases with decreasing grain size



Theoretical breakthrough curves (solid line, resp. dotted line) and experimental breakthrough curves of transport: ^{3}H (,), Se(IV)(Δ,), Se(VI) (,) a ^{85}Sr (,) in crushed granite (blank symbols) and in fracture infill materials (filled symbols) with grain size 0.125 – 0.63 mm in synthetic granitic water

Planned experiments

- Study of migration behavior of bentonite colloids using column experiments
- Study of migration behavior of radiocolloids (^{85}Sr) using column experiments