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Testing Suitability of Zerovalent Iron Materials for Reactive Walls

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Environmental Context

Groundwater remediation is mostly a costly long-term process. In-situ remediation by permeable reactive barriers is a potential solution. For pollution by various redox sensitive contaminants, zerovalent iron (ZVI) has been proposed to immobilise or degrade dissolved pollutants in groundwater. Scrap iron materials are considered as an effective low-cost ZVI material. Due to the wide variation of scrap metal compositions, testing methods for characterising the corrosion behaviour need to be developed.

Abstract

Zerovalent iron (ZVI) has been proposed as reactive material in permeable in-situ walls for contaminated groundwater. An economically feasible ZVI reactive wall requires cheap but efficient iron materials. From an uranium treatability study and results of iron dissolution in 0.002 M EDTA by five selected ZVI materials, it is shown that current research and field implementation is not based on a rational selection of application-specific iron metal sources. An experimental procedure is proposed which could enable a better material characterization. This procedure consists in mixing ZVI materials and reactive additives including contaminant

releasing materials (CRM) in long term batch experiments and characterise the contaminant concentration over the time.

Key Words: contaminant, groundwater, in-situ remediation, zerovalent iron, uranium.

Introduction

Groundwater contamination is one of the most difficult and expensive environmental problems.[1, 2, 3] The most common technology used for remediating groundwater has been to pump the water and treat it at the surface (pump-and-treat technology).[4] Reactive permeable barriers are discussed as economically preferable alternatives.[5, 6, 7] Permeable reactive walls have been developed for various pollutants. Operating permeable reactive walls treat contamination as halogenated hydrocarbons, chromium, nitrate and uranium.[1, 3, 8-10]

A permeable reactive wall is constructed from appropriate treatment media (mixed with sand and) installed downgradient of a pollution source perpendicular to the groundwater flow direction to immobilise or degrade dissolved pollutants.[11] The mitigation effect on the pollutant has to be assured for the entire lifespan of the treatment system. The most commonly used reactive material is granular ZVI. ZVI walls are assumed to be active for several decades,[1, 3] even though the long-term reactivity of these materials is currently under investigation[12-15].

The remediation property of ZVI (Fe^0) materials is based on the standard potential of the couple of Fe^0/Fe^{2+} (– 0.440 V). This negative potential enables ZVI to act as a reducing agent relative to several redox-labile compounds. Furthermore, the solubility of Fe^{2+} in water depends on both pH and redox potential. Decreasing E_H and pH increases the solubility of Fe^{2+}.[16] The oxidation of Fe^{2+} involves solid products on ZVI at neutral or basic pH, the generated precipitates can then lower the reactivity of ZVI materials. The specific surface area of solid iron (ZVI) has a direct influence on the number of active surface sites presented to the

groundwater plume.[17] These active surface sites (provided that they are available) play an important role for the initialisation, mediation and course of decontamination reactions, irrespective from the nature of the pollutant. Additional intrinsic reactivity factors for a ZVI material include: iron content (%), content of alloying elements (e.g. C, Cr, Ni, P, S), material grain size and shape, manufacturing process (e.g. raw material, heat treatment).[18-22] Beside the enumerated intrinsic reactivity factors, the groundwater chemistry and constitution plays an important role for the ZVI corrosion process and the formation of precipitates. Despite the large number of these reactivity factors for ZVI materials, no systematic study exists that address them and enable a rationale test of the fitness-for-purpose of a given ZVI material.

The suitability of ZVI for mitigating concentrations of organic and inorganic pollutants has been discussed.[8, 12, 15, 23] Previous works attempted to relate corrosion rates and efficiency towards contaminant removal of different types of iron materials to their elemental composition and surface properties (specific surface area, oxidation state).[15, 23] However, the current approach consists in testing available materials for their removal efficiency mostly for one contaminant and selecting the one showing the best removal efficiency.[15, 23, 24] This purpose is complicated in short term laboratory experiments by two key factors that have been found to influence the interaction of ZVI materials with contaminants: the oxidation state of the iron surface and the presence of corrosion products on it. [23, 25, 26].

Considering the discrepancy between short experimental time spans in laboratory (some days or weeks), the expected lifespan of a reactive wall (several decades) and the diversity of intrinsic factors capable at influencing ZVI reactivity, it is important to investigate the metallic iron (ZVI) post reactivity over this initial phase of the barrier implementation.

The aim of this paper is to propose an experimental method efficient at: (1) characterizing the reactivity of a ZVI for field application irrespective from the nature of the pollutant, and (2) investigating the long term reactivity of ZVI under specific conditions using reactive materials (natural or synthetic) to create simulated conditions.

Two kinds of not shaken batch experiments have been studied comparatively for the ZVI materials. First, the uranium removal potential was investigated over a period of two weeks. Second, the iron dissolution in 0.002 M EDTA was investigated over a period of three days.

Experimental Section

Iron Materials: One scrap iron (ZVI1) and four commercially available iron materials (ZVI2 to ZVI5) have been tested in the present study. Table 1 summarizes the main characteristics of these materials and table 2 their elemental composition. Before used ZVI1 and ZVI5 (table 1) were crushed and sieved; the size fraction 1.0-2.0 mm was used without any further pretreatment. The specific surface area of the materials were not available nor determined. This parameter is known as one of the most important reactivity factors[17, 24]. However, it is not the objective of this study to investigated the impact of the specific surface area on the reactivity of the material, but rather to compare the material in the form in which they could be used in field applications. Therefore, all other materials were use as obtained. Crushing and sieving ZVI1 and ZVI5 aimed at working with materials of comparable particle sizes. The materials differ regarding their characteristics such as content of metallic iron, additives, grain size and shape. No information about the manufacture process (e.g. raw material, heat treatment) was available.

Uranium removal experiments: To assess the effectiveness of the tested iron materials to remove uranium from aqueous solution, not shaken batch experiments were carried out. In each experiment, 0.3 g of ZVI was allowed to react in sealed sample tubes containing 20.0 mL of an uranium solution (0.084 mM) at laboratory temperature (about 20 °C) for two weeks. All experiments were conducted with the tap water of the city of Freiberg (Saxonia, Germany) of initial pH 7.2. Since the experimental vessels were not shaken, the tap water was chosen because it contains corrosion promoters such as chloride and carbonate ions (7.7 and 88.0 mg/L respectively).[18, 19] The used tap water is also a good simulator for local

groundwater.[26] Analysis for uranium was performed after reduction to U(IV) with the Asernazo III method.[27, 28]

Uranium was tested as redox-labile pollutant, that may be reduced by ZVI from soluble U(VI) species to less soluble U(IV) phases. In general, the solubility of U(IV) phases is lower than that of U(VI) phases and U(IV) phases are stable over a wider range of pH.[26] Uranium may be adsorbed onto iron corrosion products.

Iron dissolution experiments: Iron dissolution was initiated by adding 0.5 g of each material to 50 mL of a 0.002 EDTA solution. The experiments were conducted at laboratory temperature (about 20 °C) in narrow beaker with 70 mL total volume. The beaker were not shaken and were allowed to react been protected from direct sunlight on the laboratory desk. The aqueous iron concentration was recorded as a function of time. Analysis for total dissolved iron was determined using FerroVer iron reagent (HACH DR/2000 Spectro-photometer Handbook, Loveland, CO). The used disodium salt of EDTA (Na_2-EDTA, Merck: M = 336.28 g/mol) was of analytical grade. EDTA is a widespread contaminant of surface water and groundwater because of its common use in industry and agriculture [29]. The interaction of metal contaminants with organic complexants may significantly influence their transport behavior in the environment.[30-32] EDTA was used in this study as reactant (complexing agent) to induce and characterise iron dissolution from several materials.

The used EDTA concentration EDTA (0.002 M) is selected as mild dissolution agent for ZVI materials and corrosion products to enable a slow and continuous dissolution. Corrosion products are usually mixture of iron (hyd)oxides (FeOOH, Fe_2O_3, Fe_3O_4). It is expected that the kinetics of their EDTA dissolution will primarily depend on their crystallinity. The kinetics of ZVI dissolution in EDTA on the other side primarily depends on: (1) the roughness and the porosity of the surface, and (2) the oxidation state of the surface (presence of rusted sites). Other factors such as crystallinity, iron impurity, morphology or the impact of thermal treatment during the material manufacture can not be appropriately

discussed with this approach. The EDTA concentration and experimental duration (3 days) were determined in primary experiments. [26, 33]

Results and Discussion

Uranium removal: Table 3 compares the percent of irreversible U(VI) fixation (P_U) by the five tested ZVI materials. The irreversible U(VI) fixation is defined as the fraction of the fixed uranium which could not be dissolved in 0.1 Na_2CO_3 after 14 hours contact time.[35] From table 3 it can be seen that P_U varies from 63 to 87 %; the increasing order of efficiency for the materials been: ZVI2 < ZVI3 < ZVI4 $\cong$ ZVI1 < ZVI5. According to this classification, ZVI5 is the best material for a field application with respect to the current selection procedure. However, when considering complex interactions in the system "ZVI – pollutant – groundwater" it is not sure whether the most reactive material will always be the most appropriate for field applications. A material that reacts rapidly yields to more corrosion products and other precipitates that possibly accelerate ZVI passivation. It can be advantageous to select a less reactive material for example ZVI1 or ZVI2 which reactivity can be increased under field conditions for long term satisfactorily remediation. Note that if a choice has to be done between ZVI1 and ZVI4, ZVI1 has the advantage of cheapness (table 1).

Two other parameters in favour of ZVI5 are his low content of Cr and Ni (table 2) and the roughness of his surface. Note that, the least reactive ZVI2 is of smooth surface and spherical form. The increasing order of roughness of the material surface is: ZVI2 < ZVI3 < ZVI4 < ZVI1 < ZVI5, this order of roughness coincides with the efficiency of the materials for uranium removal. Thus, it is difficult to say which intrinsic reactivity factors are tested in short term laboratory experiments regardless how they will interact with extrinsic factors (groundwater geochemistry). As concerning the oxidation state of the surface, ZVI1 and ZVI2 were visually covered with corrosion products whereas the three other materials maintain

their metallic glaze. It can be emphasized that the more reactive a material is, the more corrosion products are available on its surface. The iron dissolution in 0.002 M EDTA enables an approximate quantification of the amount of corrosion products.

Iron dissolution: The basic idea of this approach is to exploit the differential dissolution behaviour of ZVI materials in 0.002 M EDTA to characterise their suitability for subsurface applications. At any datum (t) after the start of the dissolution experiment (t_0), the total iron concentration ($[Fe]_t$) as defined in Eq. 1 can be described as a function of time. It is expected, that for a certain time frame after t_0, the total aqueous iron concentration will be a linear function of the time (Eq. 2).

$$[Fe]_t = [Fe^{2+}] + [Fe^{3+}] + [FeEDTA^{2+}] + [FeEDTA^{3+}] \qquad [1]$$

$$[Fe]_t = a * t + b \qquad [2]$$

The time frame for which the linearity of Eq. 2 is assured was three days.[33] The regression coefficients "a" and "b" in Eq. 2 can be used to characterise the individual materials. In fact, "a" can be defined as the rate of Fe dissolution (from ZVI and/or corrosion products) whereas "b", the iron concentration at t_0 (ideally zero; $b = [Fe]_{to}$), can give an estimation of the amount of corrosion products on the material.

Figure 1 compares the rate of iron production for tested ZVI materials (ZVI1 to ZVI5). The corresponding regression parameters are listed in table 3. From figure 1, it can be seen that the couples (ZVI2, ZVI3) and (ZVI4, ZVI5) exhibit very closed dissolution performances in 0.002 EDTA, ZVI1 apparently been the most reactive. It was shown elsewhere, [25, 33] that the reactivity difference between ZVI1, ZVI4 and ZVI5 is due to the presence of more corrosion products on the surface of ZVI1 as confirmed by b-values in table 3. After washing ZVI1 with 0.002 M EDTA for 14 hours, it was observed that the three material (ZVI1, ZVI4, ZVI5) exhibit almost the same dissolution efficiency. The increasing order of reactivity in 0.002 M EDTA was: ZVI2 < ZVI3 < ZVI1, ZVI4, ZVI5. This classification suggests that for a field application after the current selection procedure, ZVI1, ZVI4 and ZVI5 are all

candidates. The best material will be the one showing the best removal efficiency with the targeted contaminant and been compatible with the site geochemistry. If all other parameters are comparable, ZVI1 will be chosen because of his cheapness.

Apart from ZVI5, the used materials were all cast irons (C ≥ 2%). Theoretically the reactivity of the materials primarily decreased with increasing Cr (and Ni) content.[18, 19, 22] This trend is confirmed by the experimental results, validating the method (EDTA-test).

Testing long term reactivity of ZVI material: It is shown that the EDTA-test can be used as a powerful screening method for a rapid material selection. The efficiency of ZVI materials as determined by the EDTA-test is found to be very comparable to that of U(VI) removal. However, since materials such as ZVI5 (1.96 % C; less than 0.02 % Cr+Ni) exhibited a very closed reactivity as ZVI4 (3.13 % C; 0.14 % Cr+Ni), it is necessary to check possible reactivity difference in long term. This objective can be achieved by mixing a fixed amount of each of these materials with a constant mass of a contaminant releasing material (CRM) in long term laboratory experiment and by characterizing the evolution of the pollutant concentration. This methodology was inspired from uranium leachability study from a natural rock.[35] The experiment consisted in mixing 0.15 g of selected additives (pyrite, dolomite) and 0.1 g of a natural uranium bearing rock in 100 mL of tap water in a vessel under oxic conditions. The system was continuously homogenized by a stream of water-saturated air. The results of this experiment is shown in figure 2.

It can be seen from figure 2 that dolomite effectively enhances uranium release whereas pyrite inhibits it considerably in the initial phase of the experiment. After 70 days the uranium concentration in the reference system and the system with pyrite was nearly the same, suggesting that the reference system has reached a steady state. By replacing pyrite with ZVI in the described experiment, it can be expected that uranium concentration remains close to zero as long as the ZVI is corroding. By conducting parallel experiments with different ZVI materials, a rationale material selection can be achieved. This method can be

denoted as "CRM-ZVI-test" for long term material characterisation; CRM is a contaminant releasing material such as the uranium bearing rock.

The "CRM-ZVI-test" can help to access and compare the long term reactivity of ZVI materials by mixing natural or synthetic contaminant releasing materials (CRM) with ZVI in long term experiments and characterizing the evolution of contaminant concentrations. By varying the amount of ZVI for a fixed amount of CMR, the long term performance of ZVI can be characterized in a more realistic way. Similarly, organics releasing polymers (CMR) can be synthesized to test the long term performance of ZVI for chlorinated hydrocarbons. It can be emphasized that synthetic polymers will have a larger application than natural materials since they are relatively easy to obtain and their reactivity can be readily controlled in the laboratory. Table 4 summarizes some parameters, that are experimentally accessible by long term batch experiments with ZVI and selected additives.

Conclusion

A systematic method for the investigation of the suitability of ZVI materials for in-situ remediation of groundwater has been outlined. The proposed method consists in long term, not shaken batch experiments with and without selected additives for the investigation of the impact of intrinsic reactivity factors on the long term reactivity of ZVI materials. This experimental tool is suitable both at selecting ZVI materials for in-situ remediation and at investigating some aspects of mineral precipitation on the long term performance of ZVI reactive barrier.

It was primarily assumed that the performance of ZVI walls would rapidly decrease as coatings of poorly conductive oxide minerals develop on the metallic iron surface (passivation). Field demonstrations have shown that ZVI walls continue to perform well over at least five years[13, 36]. To explain these observations, it is speculated that either the reactivity is maintained in localized corrosion pits,[26] or that new redox-active mineral phases may

function as semiconductors or electron transfer mediators.[37] The proposed experimental approach can help to bring clarity in this specific question by mixing ZVI with redox-active mineral phases (e.g. FeS) and/or by examining ZVI materials after long term batch experiment.

Further, this paper has shown the limitation of current testing methods to address the complexity of intrinsic factors, which are known to influence iron corrosion (specific surface, surface state, elemental composition, manufacture process…). Even with the proposed method, additional efforts to understand the hydrogeochemical evolution of a ZVI barrier system are required. It has been recognized for instance that information pertaining to ZVI barrier longevity is sparse.[13] Available data focus solely on geochemical factors affecting iron surface passivation.[13, 14, 36, 38] For example hydrocarbonate is corrosive to ZVI resulting in a disruption of the surface passivation and additional "consumption" of ZVI. [24] However, the increased corrosion of iron leads to a higher amount of iron precipitates and subsequently to mineral precipitation, both of them causing cementation and decreased permeability of the iron wall. Finally, this deterioration of the ZVI material ends in slower contaminant removal. Thus, the compatibility between the iron material and the subsurface has to be checked very carefully for any individual project. Investigating the intrinsic parameters affecting material corrosion with the proposed methodology will contribute to this effort.

Practical studies are to be conducted for organic and inorganic pollutants to better understand the relations between corrosion product generation, contaminant removal, mineral formation, reactivity of ZVI materials and permeability of the barrier. Ultimately, this information will aid in improving the efficiency of barrier implementation and operation.

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Table 1: Main characteristics and costs of tested ZVI materials.

origin	original denotation	code	form	Æ (mm)	Cost [a] [EURO/t]
MAZ, mbH	Sorte 69	ZVI1	fillings	-	40
Würth	Hartgußstrahlmittel	ZVI2	spherical	1.2	400
Hermens	Hartgußgranulat	ZVI3	flat	1.5	225
G. Maier GmbH	Graugußgranulat	ZVI4	chips	-	270
ISPAT GmbH	Schwammeisen	ZVI5	spherical	9	150

[a] from ref. 26

Table 2. Elemental composition of iron materials used in this study.

Material	elemental composition (%)								
	C	**Si**	**Mn**	**P**	**S**	**Cr**	**Mo**	**Ni**	**Fe**
ZVI1	3.52	2.12	0.93	n.d.	n.d.	0.66	n.d.	n.d.	n.d.
ZVI2	3.39	0.41	1.10	n.d.	0.105	0.34	n.d.	0.088	n.d.
ZVI3	3.13	0.17	0.42	0.053	0.065	0.16	n.d.	0.23	n.d.
ZVI4	3.13	2.17	0.36	0.022	0.029	0.077	n.d.	0.056	n.d.
ZVI5	1.96	0.12	0.09	0.027	0.14	0.003	n.d.	<0.001	n.d.

(*) n.d. = not determined

Table 3: Comparison of the rate of iron production (mM/h) in 2 mM EDTA, the amount of corrosion products on the materials, and the percent of irreversible U(VI) fixation (P_U) by tested ZVI materials. C and "Cr + Ni" are the carbon content and the addition of Cr and Ni contents respectively. ΔP_U gives standard deviations of the triplicates.

ZVI	C	Cr + Ni	a	b	P_U	ΔP_U
	%	%	[mM/h]	[mM]	%	%
ZVI1	3.52	0.66	1.95	19.20	81	2
ZVI2	3.13	0.39	1.54	3.43	63	5
ZVI3	3.39	0.43	1.55	5.72	71	2
ZVI4	3.13	0.14	1.82	11.32	80	2
ZVI5	1.96	0.02	1.86	13.70	87	4

Table 4: Some examples of parameters accessible by long term batch experiments with zerovalent iron (ZVI) and selected additives. t_0 is the date of the beginning of the experiment. CP = corrosion products; CRM = contaminant releasing material.

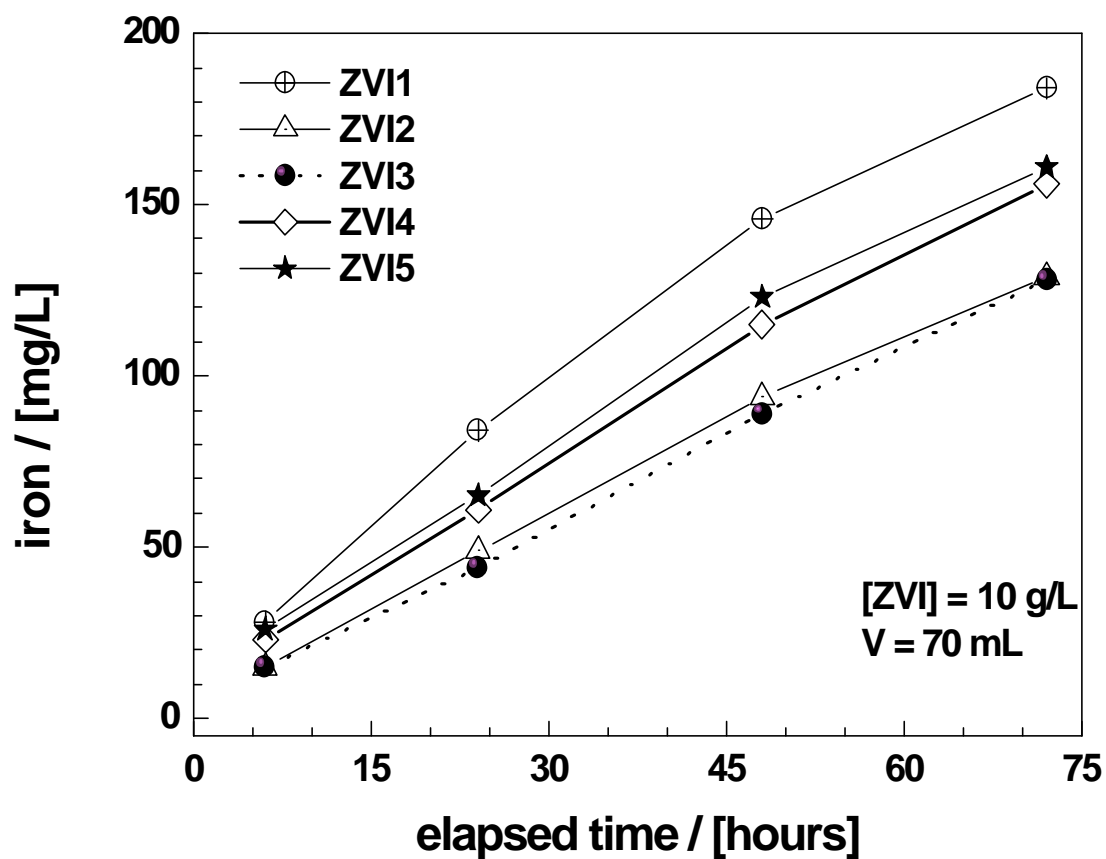| parameter	additive	date	conclusions
corrosion products on ZVI	none	(t_0), $t > t_0$	barrier performance
minerals on ZVI	$CaCO_3$, $MgCO_3$, FeS	t_0, $t > t_0$	barrier performance
groundwater constituents	Cl^-, SO_4^{2-}, HCO_3^-, HS^-	t_0, $t > t_0$	barrier performance
long term reactivity	CRM	t_0, $t > t_0$	barrier performance

Figure 1: Comparison of the iron dissolution rate by the tested ZVI materials for 72 hours.

ZVI1 is the scrap iron. The represented lines are not fitting functions, they just

joint the points to facilitate visualization. The regression parameters (a and b) are
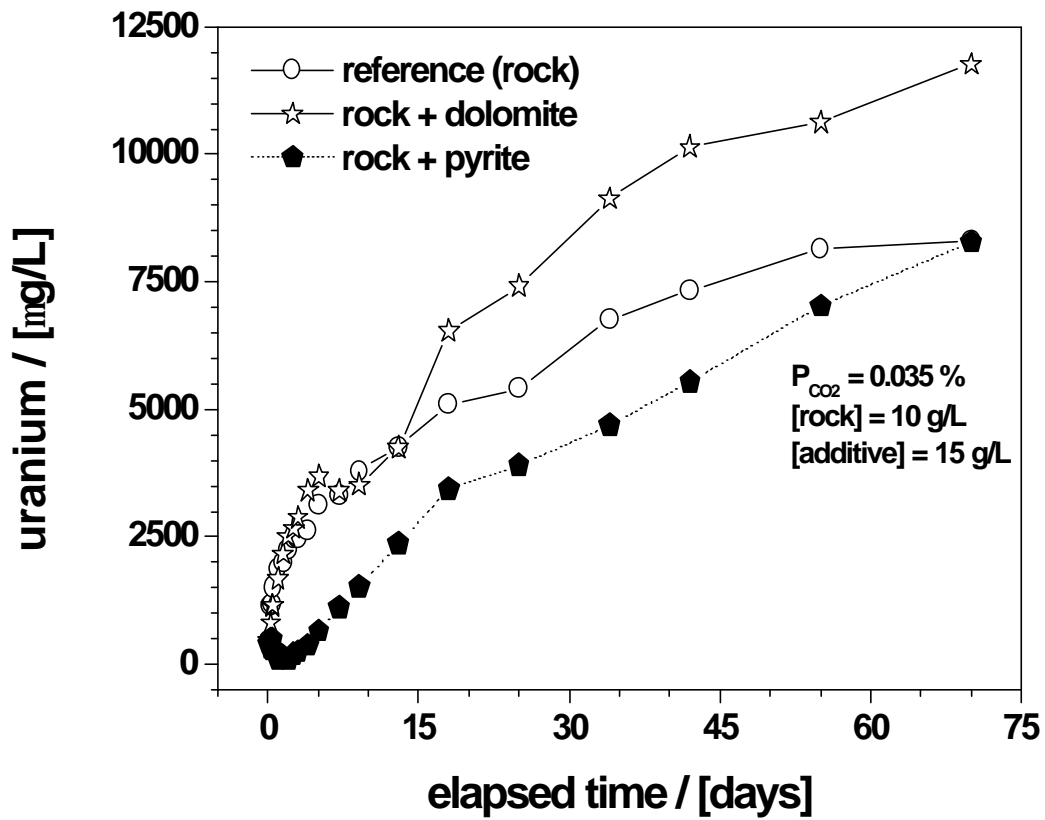
listed in Tab. 3.

Figure 2: Impact of dolomite and pyrite on the evolution of uranium concentration as
function of time in an air homogenized batch experiments for 70 days. Uranium is
leached from a natural rock as described in ref. 36. P_{CO2} is the atmospheric partial
pressure of CO_2 (open system). The particle size of used materials was: $0.315 \le d$
(mm) ≤ 0.63. The represented lines are not fitting functions, they just joint the
points to facilitate visualization.