

Application of Zero-Valent Nanoparticles for Acid Mine Water Remediation

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Abstract

The acid mine water emerged by *in-situ* chemical leaching of uranium is characterized by a low pH and by an elevated concentration of total dissolved solids (TDS). Addition of zero-valent iron nanoparticles (nanoFe⁰) involves the system ORP and the pH changes resulting in immobilization of inorganic components including toxic metals. Addition effect of two different types of nanoFe⁰ and NaOH into acid mine water solutions were compared. The concentrations of the majority of surveyed contaminants in acid solutions were lowered. The reasons of these concentration decreases and differences in reaction mechanisms of both nanoiron types were to a certain extent elucidated.

Key words: nanoparticles, nanoiron, immobilization, AMD, mine water, trace metals, uranium

Introduction

Mining activities in general cause environmental problems related to the production of acid mine drainage waters. The *in-situ* chemical leaching of uranium provided by injection of sulfuric acid results in a special type of acid mine water. This acid mine water is characterized by a low pH, typically below 2, and by a high concentration of TDS caused mainly by contaminants like sulphates and further nitrates, phosphates, aluminium, ammonium and with minor amounts of zinc, uranium, nickel, manganese, vanadium, chromium, arsenic, copper, cadmium and others. For the laboratory experiments mine water from the Straz pod Ralskem mining area was taken. The *in-situ* chemical leaching was applied on an area of 6.3 km² for over 30 years. Totally, during the period of exploitation, 4.10⁶ tons of sulfuric acid, 3.10⁵ tons of nitric acid, 10⁵ tons of ammonia and 26.10⁴ tons of fluoric acid were injected into the underground.

Application of zero-valent iron nanoparticles (nanoFe⁰) is one of the challenging technologies to examine. Beside *in-situ* dechlorination of organic chlorinated compounds (Zhang 2003), it is possible to use the nanoFe⁰ as a reductive agent to involve the system ORP decrease. This leads to a contaminant oxidation state decrease with a process of formation of a matter less soluble, less mobile or even less toxic. Moreover, nanoFe⁰ exhibits alkaline reaction with water, which is available for neutralization of acidic water. Such processes involve mechanisms like reductive mineral precipitation and co-precipitation, insoluble hydroxide formation, and adsorption. These mechanisms have already been evaluated e.g. for Al, Cd, Mn, As, Zn, Ni (Wilkin and McNeil 2003). Compared to macroscopic zero-valent iron, nanoFe⁰ has significant advantages. The specific surface of nanoFe⁰ is much higher (about 30 m²/g), which increases the reaction rates of the processes. Nanoparticles are so small that they can get through the pores in aquifer material and are transported in groundwater. For the reasons of higher or lower reactivity or mobility, the nanoFe⁰ particles can be modified in a number of ways.

The aim of series of equilibrium and kinetic experiments with nanoFe⁰ was to prove the applicability of this method on selected contaminants, to assess the properties and the reactivity of both nanoFe⁰ types and to determine the ideal properties of nanoFe⁰ fundamental for the adjustment of CS-Fe⁰ nanoparticles to this purpose.

Methods

Materials

The laboratory experiments were conducted with two samples (A and B) of acid mine water from Straz pod Ralskem. The waters originated from different leaching fields but in both cases from the most contaminated parts of the area. For evaluation of the method in different stages of remediation, the mining water samples were diluted by deionized water to get samples with various mineralization. The initial solutions were diluted by factor of 5, 10 and 25.

Table 1 Composition of non-diluted and 5x and 10x diluted mine water samples

	pH	κ	F	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	PO ₄ ³⁻	Cl ⁻	NO ₂ ⁻	U	As	Be	K	Al	Mg	Cr	Cd	Mn	Cu	Ni	Pb	SiO ₂	Na	V	Ca	Zn	Fe
		mS/m	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
A	1.82	1820	x	21400	308	272	264	36.5	8.83	29.48	3.75	0.821	51	3650	72.7	8.13	0.361	18.1	8.61	16.1	0.065	50.2	27.2	13	354	50	973
A5	2.56	477	8.87	4190	65	73	35	<10.0	<0.20	6.16	0.823	0.2	10.2	730	13.7	1.7	0.068	3.06	1.95	3.36	0.16	11.2	<0.5	2.66	67.6	11.2	184
A10	2.68	292	6.43	2180	33.6	44.7	12.8	<5.00	0.4	2.511	0.337	0.0894	3.4	351	7.1	0.859	0.033	1.86	0.834	1.75	0.065	7.2	<0.5	1.31	33.3	5.53	104
B	1.83	1280	13.8	12600	215	175	133	23.4	3.84	19.32	2.48	0.282	22.3	1810	22.4	5.18	0.157	6.1	0.725	8.1	0.026	25.1	10.9	5.64	142	29.9	607
B5	2.5	330	7.72	2260	41.6	48.5	18.6	<10.0	<0.20	3.77	0.337	0.0796	14.3	369	6	1.13	0.024	1.18	0.397	1.78	<0.010	5.1	<0.5	1.19	37.5	7.26	121
B10	2.66	205	5.08	1110	23.2	33.7	9.15	<5.00	<0.20	1.537	0.199	0.0382	1.4	178	2.4	0.557	0.01	0.656	0.118	0.919	0.056	3	<0.5	0.571	12.6	3.31	63.1

Two types of nanoFe⁰ were evaluated in the experiments. Most of the experiments were conducted with TODA (TODA KOGYO Corporation, RNIP-10E) nanosized zero-valent iron (hereafter TODA) delivered in a water solution. Some experiments were performed with newly prepared core-shell α -Fe-FeO nanoiron (hereafter CS-Fe⁰) made in a dry way of natural ferrihydrite (Fe₂O₃.nH₂O)(Filip et al.). This precursor is obtained from the waste mine water in the locality of Zlate hory. The CS-Fe⁰ for this survey was adjusted with the aim of lower reaction rates and higher particle mobility in aquifer.

Acid-base titration experiments

For the evaluation of the neutralization capacity, a potentiometric titration of 25x diluted samples (A25 and B25) was accomplished. A volume of 125 ml of acid mine water sample was titrated stepwise with 0.1M NaOH as the neutralization agent.

Batch experiments with nanoFe⁰

The aim of these neutralization batch experiments was to note the pH, ORP and conductivity change and also the changes in solution composition due to the addition of elementary iron. At first the analyses of the above mentioned initial parameters of non-diluted, 5x and 10x diluted mine waters were carried out. Subsequently, into each 1l sample in a 1l reagent bottle, an amount of 1g of the TODA nanoFe⁰ was added and the bottle cap was sealed by parafilm. The samples prepared in this manner were put on a vertically rotating shaker and were agitated (0.5 rpm) for ten days. Subsequently, chemical analyses to ascertain the final system status were implemented.

Batch experiments with NaOH

The methodics of these experiments was very similar to that of the one mentioned above. An appropriate amount of NaOH stock solution (1.91 mol/l) was added to the 1l reagent bottle of mine water in a way that the pH equilibrium after NaOH addition was equal to the final pH determined after nanoiron addition.

Kinetic experiments

Kinetic experiments were accomplished with both nanoFe⁰ types. 200 ml of 5x and 10x diluted mine water samples (A5, A10, B5 and B10) were poured into 250 ml reagent bottles and the agitation on a horizontal shaker (220 rpm) and automatic recording initiated. NanoFe⁰ (0.2 g of CS-Fe⁰ or 1 ml of TODA nanoFe⁰ stock suspension corresponding to 0.2 g of solid TODA nanoFe⁰) was added into each solution at time t = 0. Throughout the experiment the electrodes were tied to the bottle top by parafilm and polystyrene to prevent the samples from contact with the atmosphere.

Results and discussion

Acid-base titration experiments

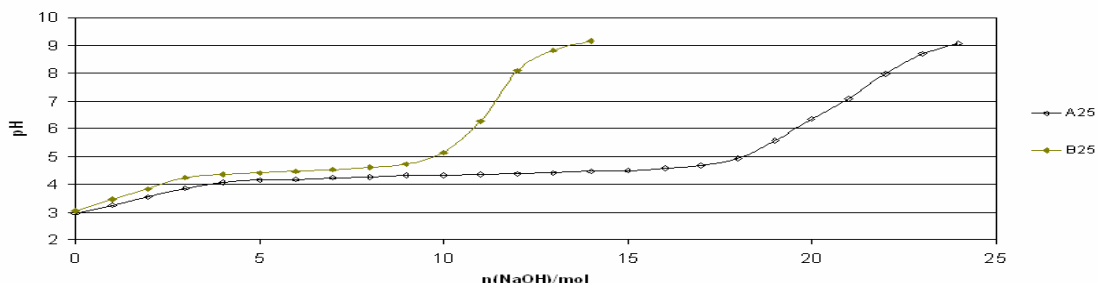
The both mine waters have a high neutralization capacity caused by big amount of TDS. With respect to the presence of a big amount of Al, we assume that the pH value between 4 and 5 is constant because beside various sulphates precipitation, an Al(OH)₃ precipitation also occurs. These verifying titration experiments proved that a consumption of big amount of neutralization agent is necessary to reach pH>7 and it results to forming an abundance of precipitates, which may cause collector permeability deterioration.

Batch experiments with nanoFe⁰ and NaOH

Final pH shifts its value due to 1 g/l nanoiron addition to graduated dial from 3.5 to 7.1 in dependence of dilution of solutions. The more multiple is the sample dilution and hence the higher is the initial pH, the bigger is the effect of the pH change owing to the same amount of nanoFe⁰. The increase effect of

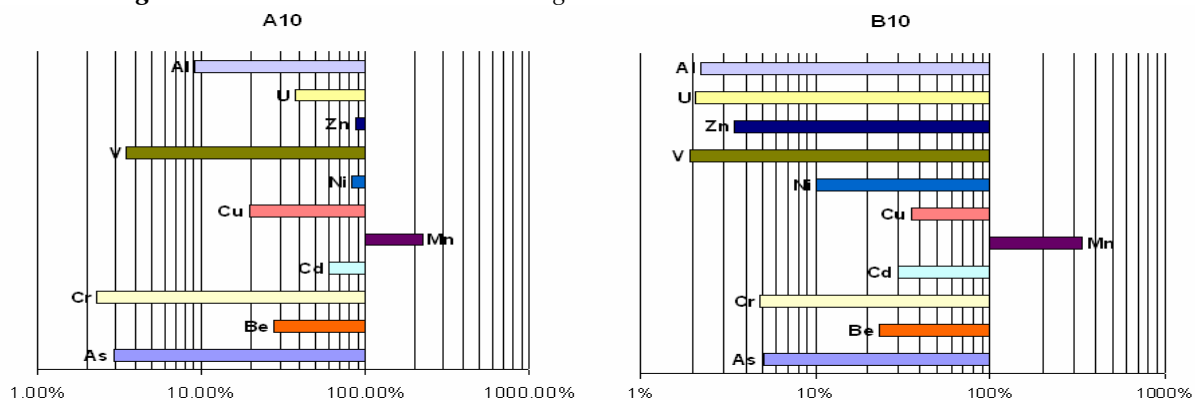
pH is bigger for the B series samples, because the salinity of these solutions is lower compared with the equally diluted A series samples. NanoFe⁰ addition has a very strong effect on ORP value and naturally the greater is the sample dilution, the bigger is the effect. Final ORP decreased to the values around 0 mV. ORP and pH changes are reflected in chemical composition changes scilicet both macrocomponents and minority contaminants. Sulphates are not too reduced by nanoFe⁰ in this case and in respect to their high concentrations appreciable changes of their concentrations do not occur.

Figure 1 Potentiometric titration of samples A25 and B25



Similarly concentrations of non-reducible ammonium ions are not influenced as well. Macrocomponent going through the biggest concentration change as a result of pH increase is aluminum. Toxicity problems of the mine water are caused by microcomponents present in low concentrations but of a high toxicity. The concentrations of the majority of these surveyed contaminants were lowered.

Figure 2 Relative concentration changes in A10 and B10 due to nanoFe⁰ addition.



Detailed mechanisms of these concentration decreases are various. For example arsenic is formed into mixed precipitates (e.g. FeAsO₄·2H₂O) on the surface of iron nanoparticles. Hexavalent uranium (U^{VI}) is reduced to the tetravalent form, which is less soluble. To the contrary manganese is at low ORP reduced from MnO₂ to much more soluble Mn²⁺ and this is why the dissolved Mn concentration increases.

Owing the appropriate addition of NaOH solution into the acid samples to reach relevant pH, the concentration decreases were comparable to the final status after nanoFe⁰ addition. No ORP changes and thus no reductive actions were occurred and this is probably the main cause of differences in mechanisms of contaminant concentration decreasing. Disadvantage of using NaOH solution is also a big amount of precipitates, which can cause well clogging during the practical application.

Kinetic experiments

The pH and ORP measurement results are demonstrated in logarithmic scale. Whereas the TODA nanoiron reacts rapidly with mine water and the pH increase after nanoFe⁰ addition is practically immediate (after one minute the pH is already above 4), the CS-Fe⁰ reaction commencement is slower. The value of about 4 is reached after more then 10 minutes from the beginning of the experiment. This delayed reaction is caused by the necessary iron adaption to the environment, a step destruction of inactive nanoparticle coat. Analogous to the pH course measurement, the ORP course was specified.

The TODA reacts rapidly again and the initial ORP decrease is namely - 200 mV in comparison with +400mV in case of CS-Fe⁰. But this decrease is only momentary and after two hours it is already at the level about 400 mV, a constant value. This increase is caused by the use-up of accessible nanoparticles and their oxidation. Generally it can be stated that owing to the stable shell around nanoparticles, there is a kinetic deceleration of interaction happening between nano Fe⁰ and acid solutions.

Figure 3 The comparison of relative uranium concentration changes in various diluted samples caused by nanoFe⁰ and NaOH addition

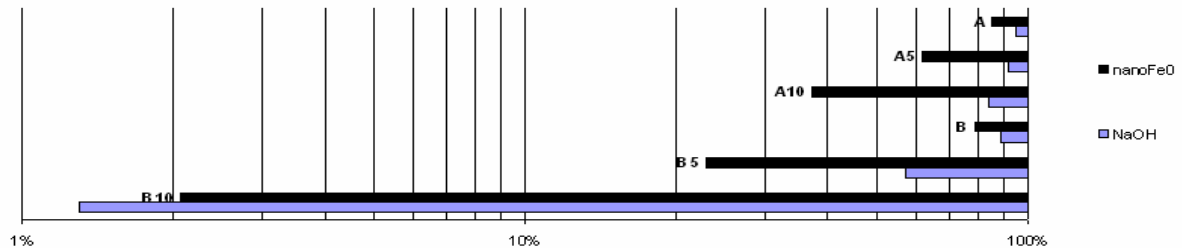
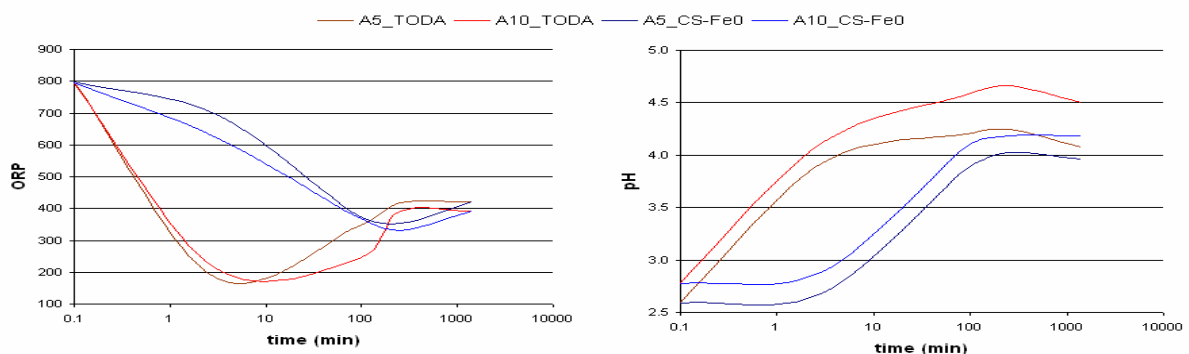


Figure 4 Kinetics course of pH and ORP during comparison TODA and CS-Fe⁰ action



Conclusions

It was proved that the addition of both types of nanoFe⁰ into acid mine water leads to an ORP decrease and a pH increase of the solutions with the consequence of changing the contaminant form and its solubility reduction. Such processes involve mechanisms like reductive mineral precipitation and co-precipitation, insoluble hydroxide formation and adsorption. And thus, the concentrations of the majority of surveyed contaminants, especially of U, V, Cr, Cu and As, were lowered.

An important nanoiron applicability criterion for the in-situ neutralization experiments is the rate of the solution pH and the ORP change after addition of nanoiron. The rapid reaction leads to a pH step change and it breeds a well clogging. Thereupon for the survey of the reaction rate of nanoFe⁰ in the environment of acid mine waters, a sample of nanoFe⁰ with thick oxidic shell, which contains 30% of total iron content, α -Fe-FeO nanoiron (CS-Fe⁰), was prepared by core-shell method. Owing to necessity of oxidic shell dissolving, the reaction of nanoFe⁰ in acid environment is slower and the initial pH and ORP changes of solution mild.

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