COMPARISON OF THE ABILITY OF LIMESTONE AND CONCRETE TO REMOVE HEAVY METAL IONS FROM CONTAMINATED WATER

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Abstract

The dissolving potential of the Ca–minerals in concrete and limestone; and precipitation potential of metal ions from model acid water has been examined with attention to change of pH during the batch tests (L/S ratio = 300 ml /0.5 g, L = model solution with M^{x+} (Ni; As; Zn; Cu; Fe) cations and $(SO_4)^{2-}$ anion). Both of materials are the source of alkalinity-generating and move pH of acid solution to alkali region. The neutralization initiates the precipitation of metal contaminants in form of insoluble compounds. It was confirmed, that concrete is able to edit pH value more significantly at test conditions than limestone (calcite) if the initial pH of water is > 1.5. Main effective compound of concrete is the portlandite – $Ca(OH)_2$. The fact that concrete generated more alkaline environment during two hours tests the metal ions have been removed from water by concrete more effectively (100 %).

1 Introduction

Industry and mining deteriorated localities are the primary sources of contaminated water. Usual pollutants of the acid mine drainage consist of heavy metal ions from sulphide minerals dissolved in water followed by pH drop to value of 2 – 3 [1-3]. In an effort to prevent releasing and spreading the pollutants the remediation technologies, e.g. the permeable reactive barriers (PRB), are being developed [4-7]. In this case, the effective reactive materials act through the chemical, physical and/or biological processes including dissolution and precipitation, sorption and oxidation/reduction. Reduction in the mobility and toxicity of metal contaminants is based on the neutralising of the acid groundwater and oxidation-reduction reactions. The contaminants are converted into the inactive states [8].

Many environmentally friendly wastes e.g. recycled concrete, limestone, calcite-bearing zeolitic breccia, blast furnace slag, oyster shells, etc. are tested for this purpose [5,9-12]. The main sources of alkalinity are some minerals e.g. anorthite ($CaAl_2SiO_8$), portlandite ($Ca(OH)_2$), calcite ($CaCO_3$). Golab et al. [4] and Obiri-Nyarko et al. [7] summarized advantages and limitations of many kinds of specific reactive materials suitable to remove contaminants.

Limestone, dolomite and lime are alkaline materials used for the acid mine drainage treatment whereas the mixture of limestone and sand is used to precipitate phosphate [9]. Limestone is rock composed mainly from calcium carbonate. The solubility of calcite ($CaCO_3$) in water establishes the ion concentration products which are $10^{-8.48}$ at 25 °C (Ks = 8.48). The solubility

of calcite in waters at ~ 25 °C ranges from $(1.3 - 5) \times 10^{-4}$ mol.l^{-1}. The pH value of solutions with calcite should be in the range of $8 - 10$ [13,14]. The removals of heavy metals by natural calcite in the aqueous solutions were studied in work [11] by evaluating various factors including calcite concentration, pH, contact time and temperature. Carbon dioxide (CO_2) dissolved in water generates carbonation. The dissolving calcite in sulphate water generates the gypsum precipitation which covers particles [15-18].

A lime (CaO) is products of the thermal decomposition of calcium carbonate which reacts vigorously with water to form a poorly soluble portlandite ($Ca(OH)_2$) ($K_s = 5.43$). The pH value of portlandite saturated solution is 12.7 [13,19].

Concrete is composed of several components including hydrated cement (i.e. $Ca(OH)_2$ – portlandite, SH – hydrated silicate, CSH – hydrated calcium-silicate and CAH – hydrated calcium aluminate), sand and gravel. A review performed by Allahverdi and Škvara [20] is devoted to the concrete degradation by acid attack. Usual pH of concrete in water is normally above 12.5. At pH values lower than 12.6 the portlandite is the first constituent starting to dissolve, followed by dissolution of the calcium aluminate hydrates. The rate of the concrete degradation markedly increases as pH of water decreases from 6.5. They found, that Al_2O_3 compounds dissolve at pH $< (3 - 4)$ while Fe_2O_3 can be dissolved at lower values, i.e. pH < 2.0. The mechanism of acid attack is complicated. The final reaction products of acid attack are the calcium salts as well as hydro-gels of alumina, silicic and ferric oxides. The gypsum ($CaSO_4.2H_2O$) formed in acid sulphated water passivates the surface of concrete particles [4,5,20].

Indraratna et al. [5] used recycled concrete as reactive material for the in situ treatment of acidic groundwater and results show that the concrete could effectively maintain near-neutral pH and remove the main contaminants.

This work compares the effect of an adding concrete and limestone into water on shift of pH value to neutral and alkali region and studies the influence of pH on removal of Ni^{2+}, As^{5+}, Zn^{2+}, Cu^{2+} and Fe^{x+} ions from water. The metal ions concentrations in the model water were derived based on acid mine drainage.

2   Experimental conditions

Crushed limestone (calcite) from the locality of Včeláre (Slovakia) and recycled concrete panels made before 1990 were used for the laboratory tests. The coarse aggregates were crushed by jaw crusher, then by edge mill and sieved to grain classes. The batch tests were performed with the particle size of $80 - 100$ μm.

The chemical composition of samples is shown in Table 1. The surface area (S_A) was measured by nitrogen gas adsorption analyser (*Quantochrome NOVA*-1000) and determined by BET method. Before the analysis, the samples have been dried at a temperature of 110 and 190 °C for 14 hours in vacuum.

The solutions containing Ni^{2+}, Zn^{2+}, Cu^{2+} and/or Fe^{2+} ions at 1, 10, 20 and 25 mg.l^{-1} concentration, respectively, were prepared using the analytical grade sulphate salts and demineralised water. The As^{5+} solution with concentration of 2 mg.l^{-1} was prepared from acid standard solution (1 g.l^{-1} of As^{5+}/HNO_3). The pH value of solutions was measured by *pH meter MS11*. The initial pH values of single and mixed solutions are listed in **Table 2.** Initial pH was adjusted to 1.3 and 2.0 by sulphuric acid in two tests only.

Table 1 Chemical analysis of limestone and concrete

Samples	Chemical composition [wt.%]							
	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	Na$_2$O	K$_2$O	Loss on ignition
Limestone	51.67	0.64	0.51	0.44	0.33	0.38	0.021	42.9
Concrete	23.32	42.83	5.1	3.54	4.7	0.59	0.54	21.02

Table 2 Concentration of M^{x+} in solutions

Salts (p.a)	Concentration of M^{x+} in solution [mg.l^{-1}]	Natural pH of solution
CuSO$_4$.5H$_2$O	20	5.3 – 5.5
ZnSO$_4$.7H$_2$O	10	5.4 – 5.9
NiSO$_4$.7H$_2$O	1	5.8 – 5.9
As^{5+}(stabilised by HNO$_3$)	2	2.9
CuSO$_4$.5H$_2$O + ZnSO$_4$.7H$_2$O + NiSO$_4$.7H$_2$O	20+10+1	5.5 – 5.6
FeSO$_4$.7H$_2$O + CuSO$_4$.5H$_2$O + ZnSO$_4$.7H$_2$O + NiSO$_4$.7H$_2$O	25+20+10+1	4.2
FeSO$_4$.7H$_2$O + CuSO$_4$.5H$_2$O + ZnSO$_4$.7H$_2$O + NiSO$_4$.7H$_2$O + As^{5+}	25+20+10+1+2	3.2

The batch tests were carried out at liquid-to-solid ratios (L/S) 300 ml/ 0.5 g at laboratory temperature. Experiments were carried out in a 500 ml glass flask on magnetic stirrer (*Heidolph MR Hei standard*) at 600 rpm. The dosage of 0.5 g sample was added to 300 ml of test solution. Sampling in amount of 15 ml was carried in times 10, 20, 30, 60 and 120 min; at the same time pH value was measured. The obtained samples were filtered. The concentrations of Ni, Zn, Cu, Fe, As, Ca, Mg, Al and Si ions in filtrates and reference solutions were measured by the inductively coupled plasma-atomic emission spectroscopy (*ICP-AES/ iCAP 6000 Series*) after acidifying by a drop of HNO$_3$.

The ability of limestone and concrete to remove Ni, Zn. Cu, Fe, As ions from model water under the conditions of the batch tests was evaluated from concentration changes of M^{x+} as follows:

$$E = \frac{C_o - C_\tau}{C_o}.100 \text{ \%} ,$$ (1.)

where: E – removal efficiency of ions from solution (wt.%), C_o (mg.l^{-1}) – initial M^{x+} ion concentration in solution (the average value of the two replicates) and C_τ (mg.l^{-1}) – concentration in time 10, 20, 30, 60 and 120 min (the average value of the two replicates).

3   Results and discussion

As it is seen in **Table 1**, the Ca content in limestone is almost two times higher than that of (Mg and Ca) in concrete. Calcium in concrete is bound mostly in the hydrated alumina-silicates, portlandite and carbonates.

The measured specific surface area of 80 – 100 μm of the grain size particle of concrete (12 – 14 m^2.g^{-1}) is ten times larger than a limestone (1 – 1.2 m^2.g^{-1}). The adsorption/desorption isotherm

from surface measuring appertain to a limestone is typical for non-micro- and non-mesoporous material (**Fig.1**). The shape and extension of hysteresis loop of concrete is associated with the capillary–shaped mesopores. The origin of the concrete porosity relates to its production; the micro- and mesopores remain in concrete after the evaporation of water. The greater surface and porosity which is characteristic for the concrete alone can be beneficial for its leaching.
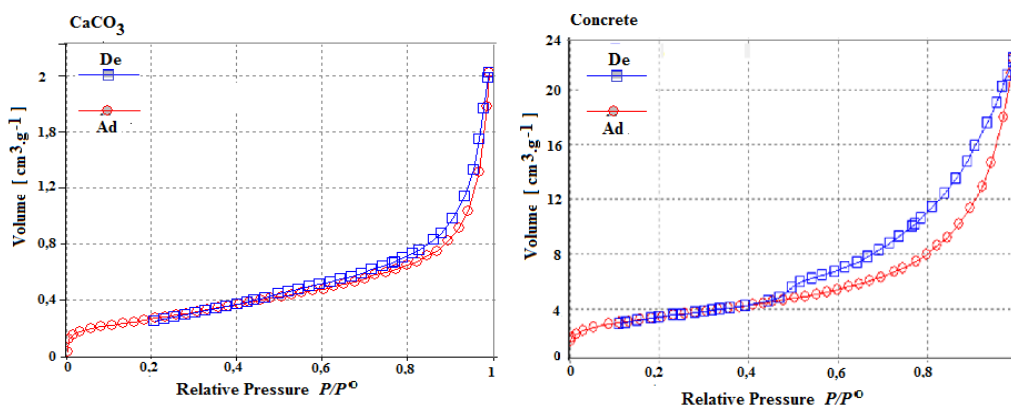

Fig. 1 Adsorption-desorption isotherm of 80 – 100 μm grain size of the limestone and concrete, ○- adsorption, □ - desorption

The addition of limestone and concrete to deionised water (0.5 g/ 300 ml) increased the initial pH (5.7) of water significantly but after 4 hours it began slightly to drop, as it is seen in **Fig. 2.**
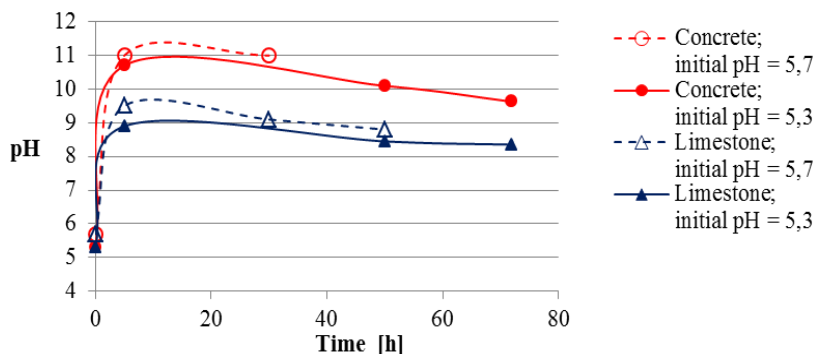

Fig. 2 Time dependence of pH change due to limestone and concrete (L/S = 300 ml: 0.5g)

Their addition to the slightly adjusted water by sulphuric acid (pH = 5.3) caused similar but more moderate changes of pH. These results confirm that the system achieves the steady-state very slowly and the process is not simple. Alkali carbonates solubility is the objective of the separate studies of several authors [15-17] and [13] refers that the addition of calcium carbonate into water caused the increase of pH to 9.93. Chemical interactions among the components in solution are driven by chemical disequilibrium that persists in the system

Ability of concrete and limestone to remove the metal ions (Ni, As, Zn, Cu) from contaminated water and change of pH demonstrate the results in **Fig. 3** and **Table 3.**

Table 3 pH value and amount of elute Ca^{2+} from limestone and concrete into solutions during 60 min of tests.

Concentration of ions in single solution	Initial pH	pH after 60 min		Concentration of Ca^{2+} after 60 min $[mg.l^{-1}]$	
		Limestone	Concrete	Limestone	Concrete
2 mg $As^{5+}.l^{-1}$	2.9	7.9	10.3	8.9	9.7
1 mg $Ni^{2+}.l^{-1}$	5.8	8.5	10.7	2.8	4.9
10 mg $Zn^{2+}.l^{-1}$	5.5	7.8	10.1	3.1	5.0
20 mg $Cu^{2+}.l^{-1}$	5.3	6.5	7.2	2.1	4.9
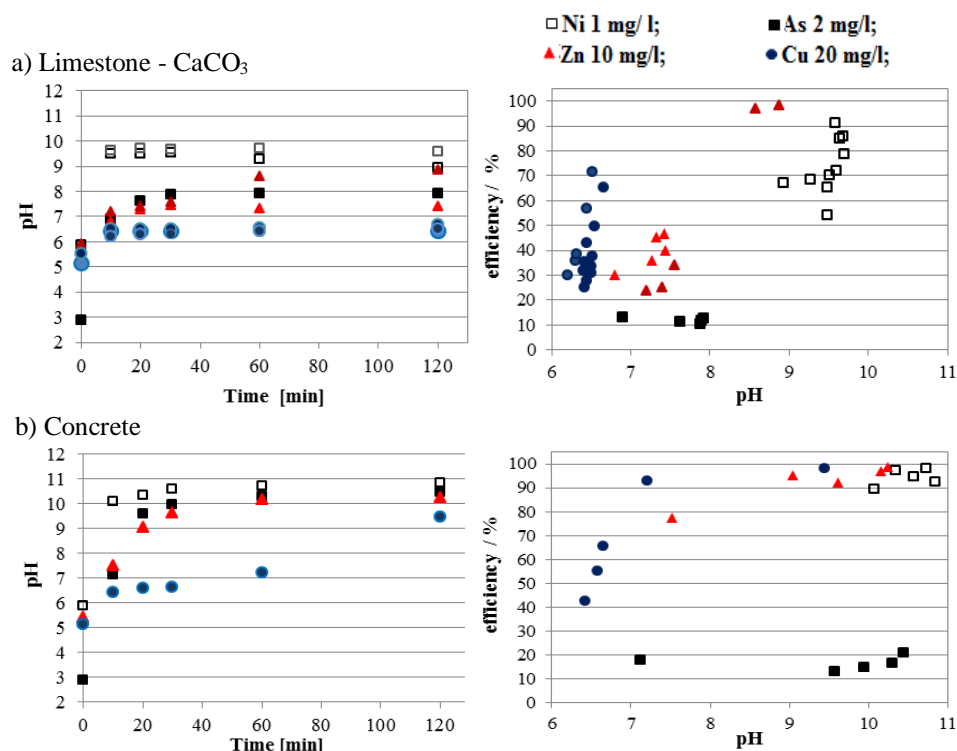
Fig. 3 Change of pH and ability of limestone and concrete to remove the metal ions from single solutions; initial concentration of metal ion in solutions:
Ni – 1 mg.l^{-1}, initial pH 5.8;   As – 2 mg.l^{-1}, initial pH 2.9;
Zn – 10 mg.l^{-1}, initial pH 5.4 – 5.9;   Cu – 20 mg.l^{-1}, initial pH 5.2 – 5.5

The results in **Table 3** show the simultaneous increase basicity and Ca^{2+} ion concentration in solution. All results confirm that pH and the Ca^{2+} ion concentrations are higher in solutions with concrete than limestone after 60 min of testing. The pH of concrete containing solution converges to 10 – 11 and limestone shifts the pH only to the value of 7 – 9.5. This shift is explained as a result of dissolution of Ca^{2+} compounds. The concrete creates a stronger basicity environment than limestone. The shift of pH to alkali region is more if a concentration sulphate in solution is higher and also milky of solution grew significantly with time.

The significant effect of pH on the removal of ion metals from water can be seen in **Fig. 3** with reproducible tests of Cu^{2+} and Ni^{2+}/limestone. Because the concrete increases the pH value of solutions more significantly it acts more effectively than limestone. The reason of progressive increasing of pH to 11 during long-time exposition is due to a composition of concretes (portlandite) [17].

The solubility of Ni; Zn; Cu; Fe and Ca sulphates, carbonates and hydroxides is compared in the **Fig. 4.** As the K_s shown, the hydroxide of Ni^{2+}, Zn^{2+}, Cu^{2+} and Fe^{3+} precipitates are more stable than carbonates. When acid waters with the high content of Fe^{x+} are neutralized, first a precipitation of $Fe(OH)_3$ ($K_{s/25°C} = 3.7 \times 10^{-40}$) begins [21]. Different solubility product constants of precipitates require control of pH to achieve optimal removal of metals. The co-/re-/precipitation of carbonates is dependent on a supersaturating $(CO_3)^{2-}/(CO_2)$ of water.

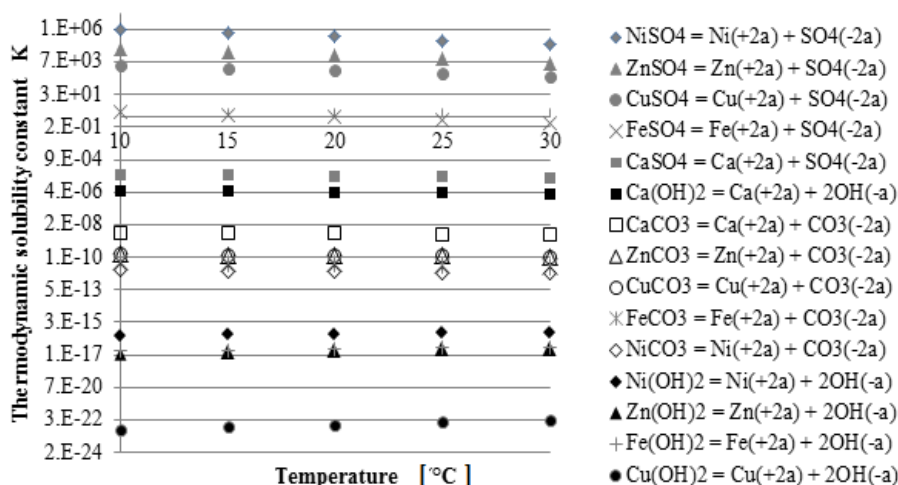**Fig. 4** Thermodynamic solubility constants (K_s) Ca–, Ni–, Zn–, Fe– and Cu–hydroxides, carbonates and sulphates calculated by HSC software vs. temperature [22]

Probable, the metal hydroxides are the dominant precipitates generated during the neutralization of acidic water. The hydroxide solubility vs. pH is illustrated in **Fig. 5**. The measured results (**Fig. 3**) are in accord with the following theoretical data in **Fig. 5**. Particular ions (M^{x+}–metal) with the concentration of 3×10^{-4} mol.l^{-1} (20 mg.l^{-1}) for Cu^{2+}, 1.5×10^{-4} mol.l^{-1} (10 mg.l^{-1}) for Zn^{2+} and 2×10^{-5} mol.l^{-1} (1 mg.l^{-1}) for Ni^{2+} precipitate at pH ~ 6; > 7.5 and > 8.5, respectively.

The releasing of calcium from limestone and concrete in sulphate water led to the formation of gypsum ($CaSO_4.2H_2O$). The thermodynamic solubility constants of $CaSO_4$ ($K_{25°C} = 5.2 \times 10^{-5}$) predict a precipitation of gypsum from solution which is saturated by $(SO_4)^{2-}$ and Ca^{2+}. The fine precipitates cover the grains and inhibit their dissolution. This complicated reaction system attains only very slowly the equilibrium state [18].

The presence of other metal ions in solution can influence the sorption and precipitation processes therefore the experiments were carried out also by mixed solution of Ni^{2+}, As^{5+}, Zn^{2+}, Cu^{2+} and Fe^{2+} ions. The results in **Fig. 6** show how the limestone converts pH to range 5.5 – 7.5 and the concrete to range 6 – 11, except the case of the batch test with initial pH = 1.3. In the case of concrete, pH 1.3 increased only on the value ~1.6. Lower content of Ca in the concrete

beside in comparison to limestone is cause of this effect. The dissolution rate depends essentially on pH and the chemical reactivity of matter and reactive surface area. The acidity of initial solution has significant influence on solubility of Ca–minerals in concrete and limestone (**Table 4**). Higher Ca^{2+} concentration in solution (initial pH 5.6) with concrete is caused by dissolution of portlandite.
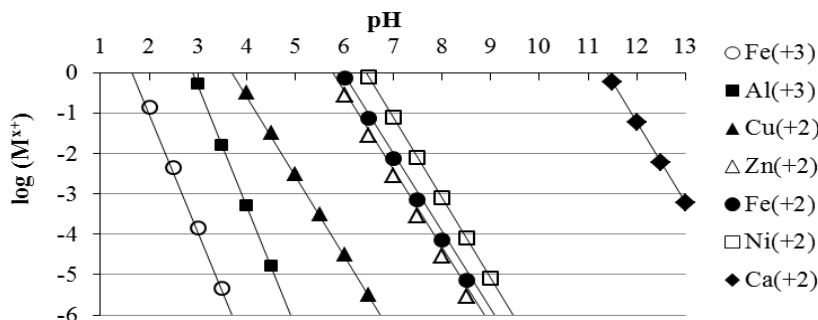

Fig. 5 Metal hydroxides solubility dependent on pH at 25 °C; data are calculated by

$$pH = \frac{\log K_{s/M(OH)_x} - \log M^{x+} - x.\log K_v}{x}$$ [23] from thermodynamic solubility constants

$K_{s/25°C}$ [22]

Table 4 Amount of Ca^{2+} released into solution during the batch test

initial pH	Limestone					Concrete				
	1.3	2.0	3.2	4.2	5.6	1.3	2.0	3.2	4.2	5.6
Time [min]	Ca^{2+} in solution / [mg Ca^{2+}/0.5 g sample]									
10	111	33.8	7.2	12.9	1.28	53.4	43.2	11.7	12.2	10.9
20	113	-	11.2	14.6	1.96	55.1	-	14.1	14.2	7.6
30	115	39.4	13.2	16.0	2.32	58.2	46.5	15.7	15.9	8.8
60	115	46.6	16.8	17.7	3.81	61.2	51.4	18.4	16.8	11.0
120	118	47.6	18.9	18.9	5.92	62.6	56.5	20.5	17.4	12.6
	~185 mg of Ca^{2+} in 0.5 g of limestone					~85 mg of Ca^{2+} in 0.5 g of concrete				

The Al^{3+} and Si^{4+} concentrations in solution with concrete increased in the first minutes of test and then the content Al^{3+} in solution markedly and the Si^{4+} moderately decreased with alkalinity. In the end, after 120 min the contents ~ 60 mg of Ca^{2+}, 3.2 mg of Fe^{x+} and 14 mg of Al^{3+} were detected in solution.

The test results with mixed solutions (Ni-(As)-Zn-Cu-(Fe)/ 1-(2)-10-20-(25) mg.l^{-1}) and with various initial pH (2; 3.2; 4.2; 5.6) are presented in **Fig. 7.** Data again confirm that the ability of concrete to remove Ni-(As)-Zn-Cu-(Fe) ions from water is more effective than limestone. The pH value of acid solution increases firstly very sharply together with the Ca^{2+} concentration and then it increases only slowly. The limestone (calcite) converted the pH approximately only to (6.5 - 7.0) during 120 minutes. Because water in preference dissolves calcium compounds - portlandite, the concrete shifted pH up to 10 – 11.
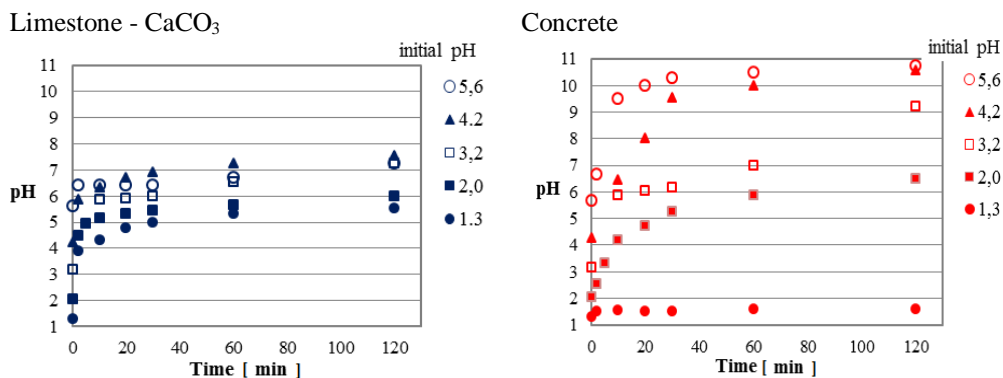
Limestone - CaCO$_3$ Concrete

Fig. 6 Changes of pH in mixed solutions during the test with dosage 0.5 g of limestone and/or concrete in 300 ml solution at 20 °C
- mixed solution of Ni-Zn-Cu (1-10-20-25 mg.l^{-1}), initial pH = 5.6
- mixed solution of Ni-Zn-Cu-Fe (1-10-20-25 mg.l^{-1}), initial pH = 4.2 ;
- mixed solution of Ni-As-Zn-Cu-Fe (1-2-10-20-25 mg.l^{-1}), initial pH= 3.2;
- mixed solution of Ni-As-Zn-Cu (1-2-10-20 mg.l^{-1}) adjusted by H$_2$SO$_4$; initial pH= 2.0;
- mixed solution of Ni-Zn-Cu-Fe (1-10-20-25 mg.l^{-1}) adjusted by H$_2$SO$_4$. initial pH= 1.3

The desirable pH value for the precipitation of Cu^{2+}, Zn^{2+} and Ni^{2+} ions from sulphate solutions is higher than 6.5; 8 and 8.5 respectively. The eminent decrease of metal ion concentration in solution after addition of concrete is not surprising in relation to achieved pH values.

The differences between the effect of limestone in mixed solution of Ni-(As)-Zn-Cu with Fe (initial pH = 4.2) and without Fe (initial pH = 5.6) are evident. The concrete in acid solution is the source of small amount of Fe ions. The results in **Fig. 7** suggest that the presence of Fe ions in solution supports the removal of As (oxid–reduction reactions Fe$^{2+/3+}$ and prior precipitation of Fe^{3+} –oxy/hydroxides). A problem of As–pollutants was studied in detail in several works [24-26].

The results of the batch tests predict the behaviour of crushed limestone and the concrete in the reactive barriers. Last but not least, it is important to know the effect of the deposition precipitates and their clogging in the barriers. This knowledge can be obtained by a long-time flow-tests or pilot-plant tests of PRB only.

Limestone – CaCO$_3$ Concrete
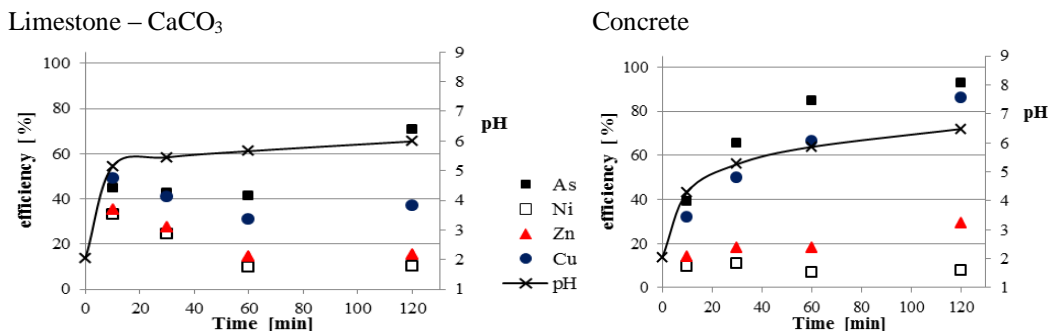
a)   - mixed solution of Ni-As-Zn-Cu (1-2-10-20 mg.l^{-1}), initial pH = 2;

b)   - mixed solution of Ni-As-Zn-Cu-Fe (1-2-10-20-25 mg.l^{-1}), initial pH = 3.2;

c)   - mixed solution of Ni-Zn-Cu-Fe (1-10-20-25 mg.l^{-1}), initial pH = 4.2 ;

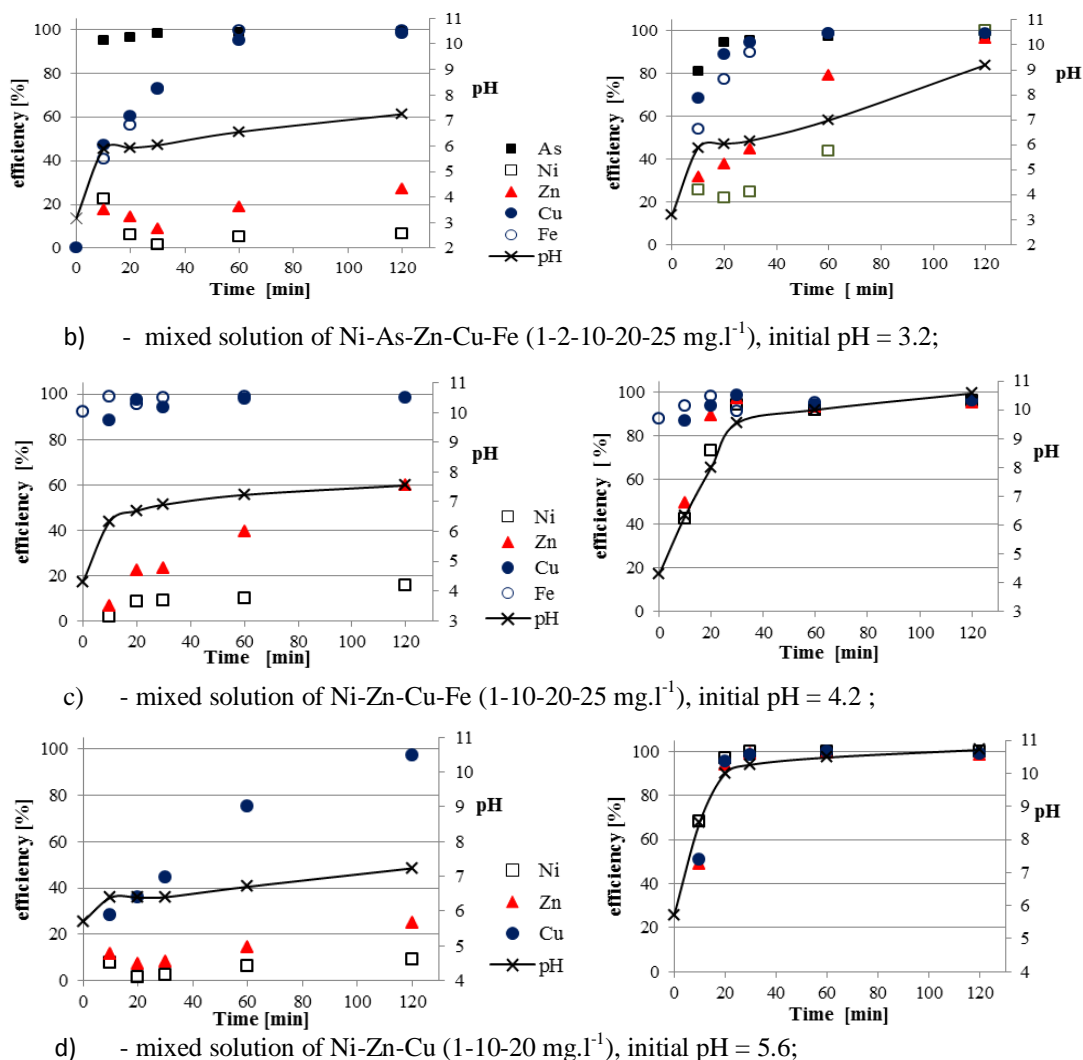d)   - mixed solution of Ni-Zn-Cu (1-10-20 mg.l^{-1}), initial pH = 5.6;

Fig. 7 Time dependence of removing metal ions from mixed solutions accompanied by pH value

4   Conclusions

An actual basicity of solution is decisive for metal ions (Ni, Zn and Cu) removal from water. The results proved that the crushed concrete increases the basicity more significantly (up to pH ~11) than limestone. It is reason why the metal ions are removed by concrete more effectively. Nevertheless, the potential of concrete to convert pH from < 2 to neutral region is lower than that of limestone. Main effective compound of concrete is the portlandite – Ca(OH)$_2$ and the limestone is calcite – CaCO$_3$. The results indicate, the softly calcined limestone could be effective still than limestone and concrete.

Even if a removal of metal from solution converges to 100 %, the test–time of 120 min is too short for the system to achieve the equilibrium state. It is evident that obtained data depend on

the condition and system configuration of test: as ratio L/S, a residence time of solution, a basicity progress/stability/regress in reaction zone, primarily.

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