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THE APPLICABILITY OF PASSIVE METHODS FOR THE PURIFICATION OF MINING WASTEWATERS IN SLOVENIA

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ABSTRACT

The results of chemical analyses of selected samples of mining wastewater from abandoned mines in Slovenia have confirmed the suspected increased metal ion content and accompanying anion content in wastewater, depending on the mineralogy of individual mines. Since the dominant rock in Slovenia is limestone, typical acid landfills and mine leachate are not found. For this reason and partly due to climatic conditions in Slovenia, the direct adoption of the established alternative technology based on neutralization - precipitation - biological decomposition would not be an ideal approach to the remediation of mine leachate in Slovenia. The aim of this study was to adapt passive methods for this specific conditions and evaluate the applicability of technical minerals existing in Slovenia for this purpose.

DEVELOPMENT OF PASSIVE TREATMENT

The capacity of various natural wetlands to break down pollutants (organic matter) is known since the 19th century. Even then, English farmers employed the cleansing potential of nearby marshes for the treatment of municipal wastewater. Water treatment tanks and various plants were more deliberately introduced on a larger scale in the USA and Canada during the thirties, and in Europe after the second World War, mainly for the decomposition of organic components in municipal wastewater.

Realising that surface and ground waters can be polluted by mine and deposit leachate even decades after the mines have been closed down, many countries on almost all continents have, during the past three decades, invested in the development of alternative methods for the treatment of mining wastewater (metal minerals, coal mines - black coal). It's important to mention that passive purification of mining wastewater did not develop as a result of experimental and laboratory work, but from monitoring the quality of water from the abandoned mines which passed through natural marshes. Further development of the passive treatment techniques of mining wastewater was based on the exploration and improvement of natural purification processes within the wetland. Passive treatment involves several techniques of creating artificial wetlands that use natural, geochemical

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mechanisms for the regulation of the water's pH and the lowering of toxic component content. Today (Kleinmann et al., 1993) the most common soft technologies in mining, depending on the characteristic of influent (acidity, alkalinity, metal ions, dissolved oxygen content), involve the linkage of neutralization phases, regulation of the pH of water with anionic limestone drains, the sedimentation of precipitated components and the zone of biological decomposition (aerobic, anaerobic wetland). In the past two years, published studies have confirmed the applicability of sorption on the natural sorbent in the passive process of purifying mining leachate contaminated with metal ions.

PASSIVE TREATMENT IN SLOVENIA

In the last decade, the first artificial wetlands for municipal wastewater were constructed in Slovenia (Urbanc, 1993). However, the passive treatment of wastewater or mine drainage (or leachate) was not previously documented in literature or mine archives in Slovenia.

The quality of mine wastewater in Slovenia

Since the dominant rock in Slovenia is limestone, there are no typical acid landfills and mine leachate, which often present a problem in the processing of metal ore or the depositing of gangue containing sulphide minerals. The pH values of the water are usually close to neutral with metal ions (Fe, Zn, Cu, Pb in selected samples of mine wastewater) in partly precipitated and nonprecipitated form.

The results of chemical analyses of selected samples of mining wastewater from abandoned mines in Slovenia (Table 1, Figure 1) and from mines in the shutdown phase confirm the suspected increased metal ion and accompanying anion content in mining wastewater, depending on the mineralogy of individual mines.

Table 1: Concentration of metal ions in selected samples of mining wastewater from abandoned mines in Slovenia and mines in the shutdown phase

Location	**pH**	**Type of water**		**Concentration of metals (mg/l)**			
		Mine	**Deposit**	**Fe_{TOT}**	**Zn**	**Cu**	**Pb**
[1]Sitarjevec	6.6	◊		13.9	5.5	0.05	0.05
[2]Šmartno-Litija	6.3		◊	3.6	0.2	0.10	0.2
[3]Cerkno-Idrija	7.1		◊	31.1	0.2	0.12	0.4
[4]Ponoviče	6.6		◊	0.05	3.7	0.55	0.5
[5]Idrija*	7.7	◊		2-14	0	-	-
[6]Mežica	7.1		◊	0.18	2.1	0.05	0.1
MAC (mg/l)**	6.5-9.0			***	2.0	0.5	0.5

Note: * Periodically increased concentration of Hg and hydrocarbons

** Maximum Admissible Concentration for river discharge

*** Maximum Admissible Concentration is function of settled substances

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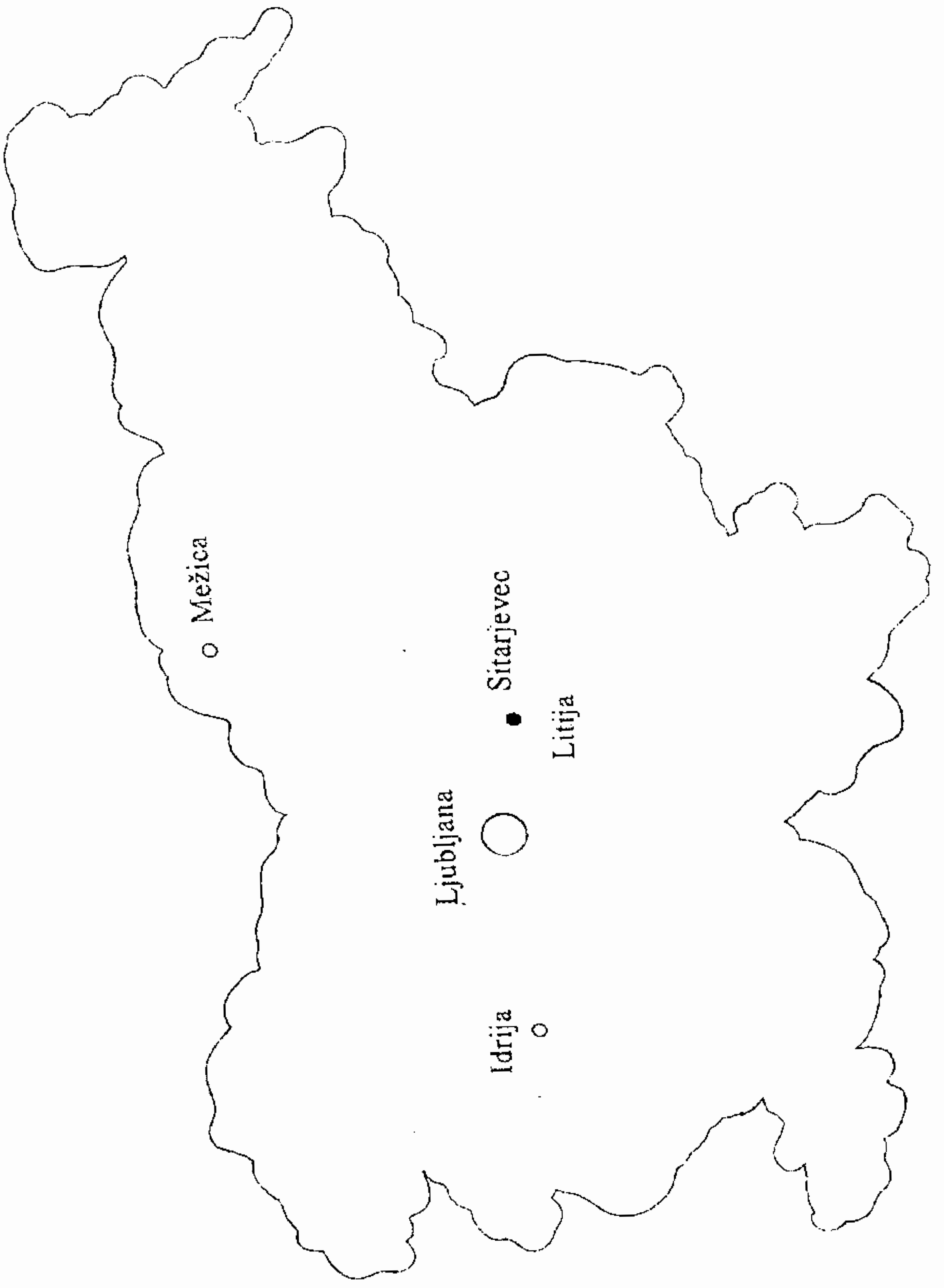

figure 1: Selected abandoned mines and mines in the shutdown phase in Slovenia

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Adaptation of passive methods to Slovenian conditions

In view of the above-mentioned facts and the climate conditions in Slovenia, the direct adoption of the established alternative technology based on neutralization - precipitation - biological decomposition would not be an ideal approach to the remediation of mine leachate in Slovenia. The adaptation of these methods to suit Slovenian conditions would ensure not only a technologically, but also an economically justifiable solution to the problem of mine wastewater wherever feasible, or add simpler methods to the conventional purifying techniques. Considering that such systems require minimum operational maintenance and that, according to financial analyses of existing systems abroad, the costs of their construction would be repaid in one year, these systems are especially suitable for abandoned mines.

As initially mentioned, the aim of the study was to adapt passive methods for the purification of mine leachate with increased metal ion content to specific Slovenian conditions and for this purpose make use of the technical minerals existing in Slovenia.The study was comprised of three parts:

- determination of the level of alkalinity of water after passage through a layer of calcite (anoxic limestone drainage or ALD), which will ensure effective precipitation of free metal ions only in the sedimentation zone,
- determination of sorption curves for metal ions in the system comprised of metal ion solution - alumina silicate (zeolite), with the aim of determining the breakthrough points or bed volume at which a consistent quality of the effluent may be expected, and
- design of model laboratory instruments for regular monitoring and determination of key parameters for evaluating the effectiveness of individual phases (pH regulation, sedimentation and sorption) in the passive process. The equations used to calculate the efficiency of real passive systems with a biological zone were adapted to allow for the calculation of the rate of contaminant (metal) removal.

Neutralization of mine water in the passive system

Passive treatment systems perform more effectively when mine drainage water has a pH greater than 6.0 and contains net alkalinity. Alkalinity neutralizes acidity (the sum of acidic properties of dissolved metal ions) and buffer changes in pH. Without the addition of costly chemicals, alkalinity can be generated by two natural processes in the passive system (Hedin et al. 1994):

- bacterial sulphate reduction which progresses in the presence of sufficient amounts of organic carbon and sulfate, producing bicarbonate alkalinity as a by-product,
- dissolution of carbonate rocks.

Limestone is the most inexpensive among the common neutralising agents used in passive systems for the pretreatment of influent before entering the biological zone (natural or artificial swam) or the sedimentation zone. As already mentioned, the primary role of ALD in passive processes is to produce alkalinity as the consequence of reactions increasing the concentration of HCO_3^- bicarbonate ions. The dissolution of calcite by evolved acid proceeds as follows (Donnovan et al., 1994):

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$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2CO_3 \qquad pH < \sim 5.3 \qquad (1)$$

$$CaCO_3 + H^+ + HCO_3^- \rightarrow Ca^{2+} + 2HCO_3^{2-} \qquad pH > \sim 7.3 \qquad (2)$$

and the dolomite dissolution as follows:

$$CaMg(CO_3)_2 + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2H_2CO_3 \qquad pH < \sim 5.3 \qquad (3)$$

Dissolved O_2 and ferric ions (Fe^{3+}) or aluminium are considered the main factors limiting the broader utilization of ALD. The dissolved oxygen concentration in mine water should be less than 1mg/l, and Fe^{3+} or Al^{3+} should be less than 2 mg/l in order to prevent the oxidation of ferrous to ferric ions and to avoid the armouring of limestone drains with oxyhydroxides. Oxygenation and the armouring of limestone particles can be reduced by covering the drainage ditch with a plastic foil or a layer of clay. Under such conditions in this anoxic environment, the metals present in raw water (particularly iron) remain in the reduced state. The ferrous iron does not oxidize and ferric oxyhydroxides contaminated with other metal ions (Mn, Pb, Zn, Cu, etc.) do not form. The metals present in the water penetrate in unaltered ionic form through the layer, despite the higher pH value of water (Nairn, et al., 1991)

Recrystalised limestone - calcite from the Stahovica open pit ($CaCO_3$ > 90%, grain size 2 – 7 mm), which fulfils the criteria for anion limestone drainage, was used in our experiment for pH regulation. The pH of acidified demineralized water (pH= 3.0 - 4.8) in dependence of the flow rate (2.5 - 6.0 $m^3/h.m^2$) of water through the calcite layer was experimentally determined (Figures 2, 3). The reduction of acidity and the formation of alkalinity titrimetrically determined using APHA Standard Methods in neutralized water samples are presented in Figures 4 and 5. The reduction of calcite mass in dependence of experimental conditions was gravimetrically determined.

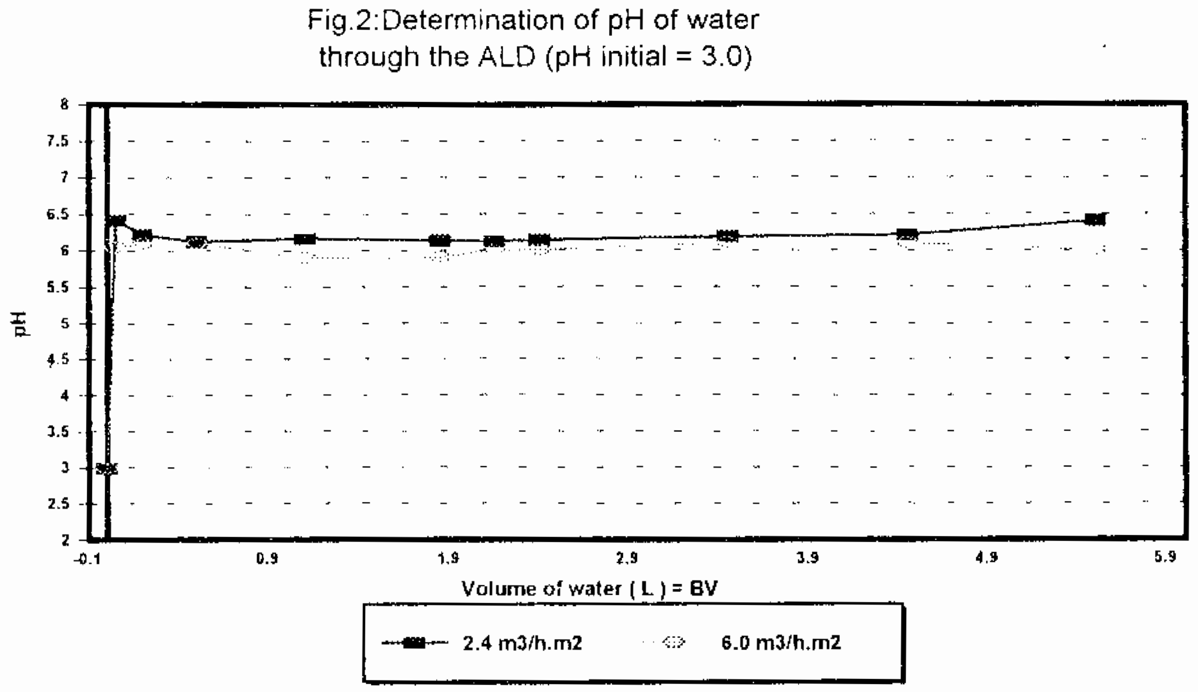

Fig. 2: Determination of pH of water through the ALD, initial pH of demineralized water = 3.0

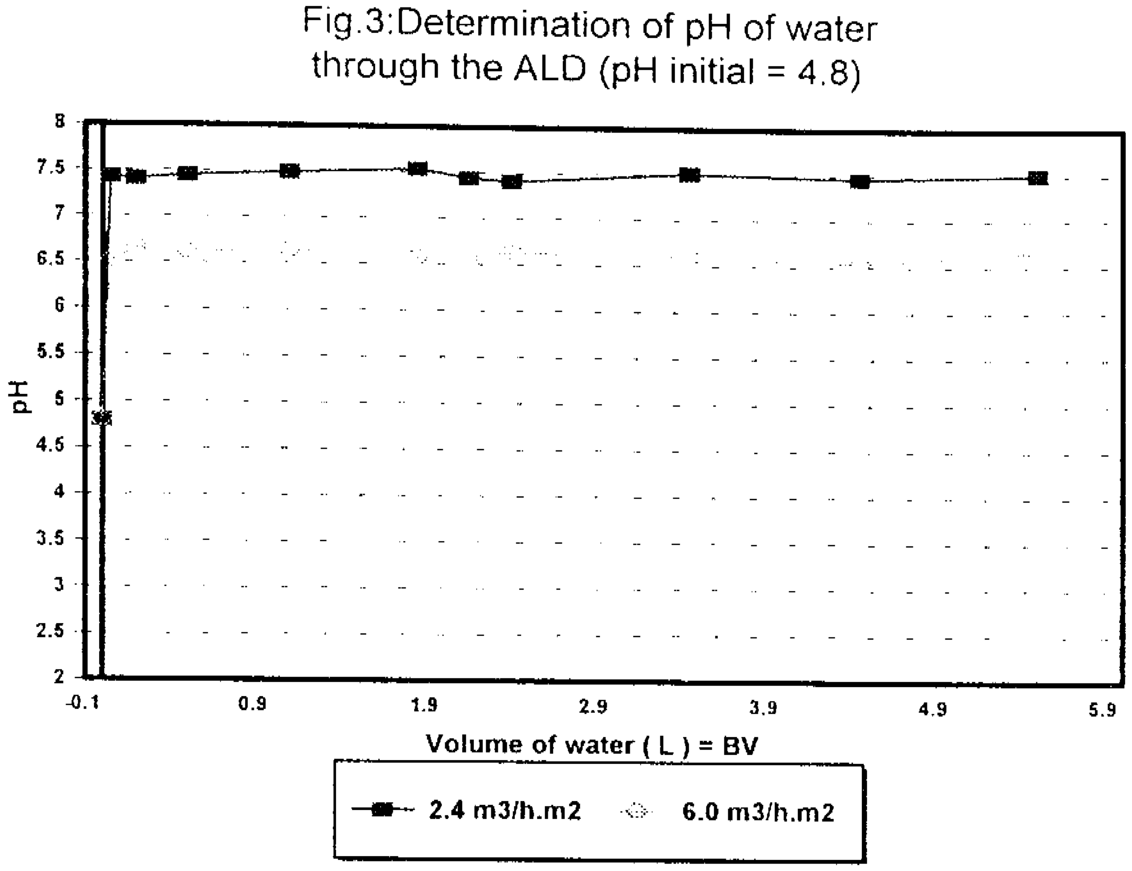

Fig. 3:Determination of pH of water through the ALD,initial pH of demineralized water=4.8

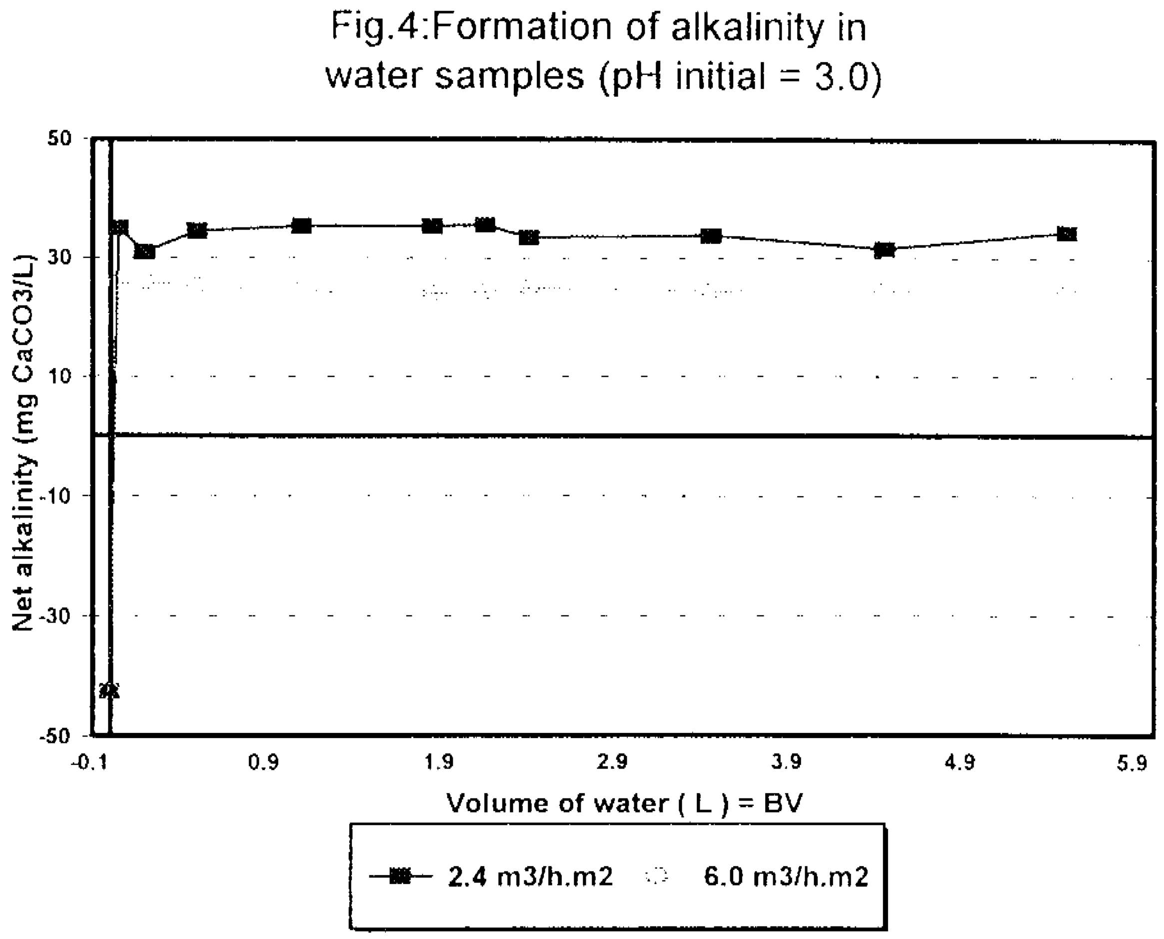

Fig. 4: Formation of alkalinity in water samples, initial pH of demineralized water =0.3

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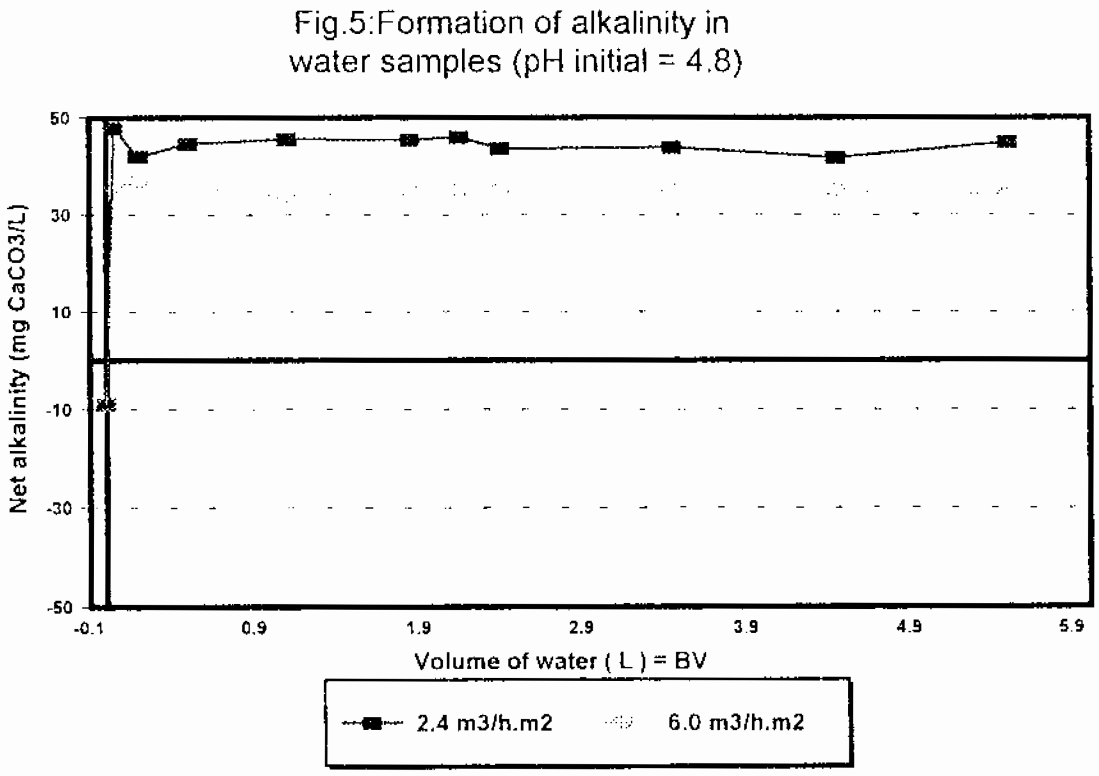

Fig. 5: Formation of alkalinity in water samples, initial pH of demineralized water = 4.8

For the zone of effluent penetration (the chosen zone corresponds to the published speed of liquid penetration in real systems, which include, apart from limestone anion drainage, the sedimentation zone and aerobic and anaerobic marshes), a pH value of 6 is achieved with selected recrystalized limestone in the acidified demineralization zone. This is the optimum value which enables, in addition to iron and aluminium, the sorption and co-precipitation of lead, zinc, copper, nickel, cadmium, etc. as hydrated oxides of iron and aluminium in the sedimentation zone with a long enough residence time (Figure 6).

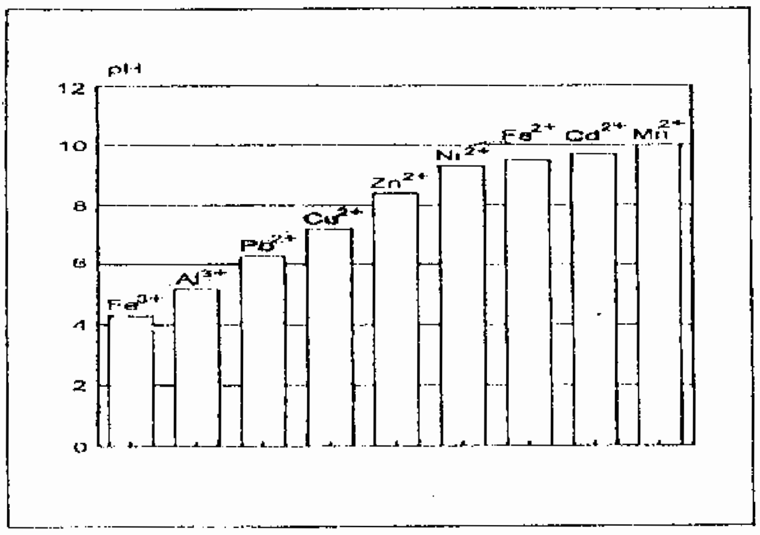

Fig. 6: pH values for metal precipitation in water solutions

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The reduction of calcite weight in the layer due to the dissolution and diffusion of hydrogen carbonate ions in the solution was below 1% under specific experimental conditions.

On the basis of experimentally obtained results relating to the applicability of recrystalized calcite from the Stahovica deposit, the following may be determined:

- during penetration through ALD, neutralization - transformation to the neutral state - was attained at all flow rates within the selected range and at all levels of acidity within the selected range. The lower the flow and the higher the initial pH of the liquid phase, the higher the pH value of the effluent.
- the net acidity decreases during penetration through the calcium carbonate layer due to its dissolution. The smaller the flow and the higher the pH value of the influent upon entry into the layer, the higher the net alkalinity of the effluent.
- under selected experimental conditions, the quality of the effluent remains constant until the entire volume of the liquid phase is purified.
- the monitoring of changes in calcite weight has shown that under selected experimental conditions, the dissolution of calcite in contact with acid solution reduced the initial weight by less than 1%. Since metal ion solutions were not yet used in this phase, the armouring of calcite grains with a layer of metal hydroxides did not occur and the hydraulic integrity of the layer remained unchanged.
- a comparison of the results obtained (Figures 2-3) with Figure 6 allows for the assumption that a pH value of 6 is that value which, under the selected operating conditions, enables the precipitation of present metal ions in the sedimentation zone. When other metal ions are also present in water together with Fe and Al, the sorption - co-precipitation of metals on hydrated oxides Al and Fe should, according to data published by other authors (Anderson et al., 1990), take place in the sedimentation zone.

Sorption on natural aluminosilicates

The pH regulation and sedimentation zones may be followed by the metal ion extraction zone employing trace sorption on natural sorbent. For this purpose clay mineral may be used. In our experiment, the columns were filled with zeolite tuff from Zaloška Gorica (50% content of zeolite minerals, mostly as clinoptilolit, heulandit and mordenite) with cation exchange values between 125 - 135 meq NH_4^+/100 mg of dry weight.

Sorption is often described in terms of isotherms, which show the relationship between the bulk aqueous phase activity (concentration) of adsorbate and the amount adsorbed at constant temperature. In column operations, the breakthrough capacity (BC) is a more useful value for defining the number of effective exchange sites. BC is that quantity of ions which bind themselves to the exchanger until their traces appear in the effluent. According to Michaels, the breakthrough point is attained when the content of pollutant in the effluent exceeds 5% of its value in the influent. The saturation of the sorbent is complete when the concentration of pollutant in the effluent reaches 95% of its value in the influent. Some authors (Keramida et al., 1983) refer to experimental evidence

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supporting the assumption that the value of the breakthrough point - total flow of influent through the zone - increases with decreasing flow rate, yet the relation is not linear. The breakthrough capacity depends on the dynamic behaviour of a system and therefore varies with the particular ions undergoing exchange, the particle size of the exchanger, the liquid flow rate and the temperature of the systems (Grimshaw et al. 1975).

Considering the fact that sorption would be the last stage before discharge into the recipient, the concentration of metal ions should be in the range of MAC or, at maximum, double MAC. In experiments aimed at determining the saturation of natural sorbent and the limit conditions for determining the optimal operation of the sorption layer, the deviations from MAC for discharge into the recipient were taken into account in addition to BC values. Figure 7 presents the experimentally obtained values at initial Pb, Cu concentrations c_0= 1 mg/l and initial Zn or Fe concentrations c_0= 4mg/l, which represent twice the value of MAC for discharge into the recipient. The liquid flow rate was within the range of 5 - 6 $m^3/h.m^2$, which corresponds to the top limit of liquid flow rate at which the efficiency of the passive procedure in a model laboratory device was evaluated. Analyses were performed until the volume of effluent reached 1000 l.

In determining the breakthrough curves, the volumes of effluent, divided by the bed volume (BV), are plotted on the x axis. As the volume of the sorbent layer was approximately 1 in our experiment, the x values in Fig. 7 designated as effluent volume, actually correspond to the BV value.

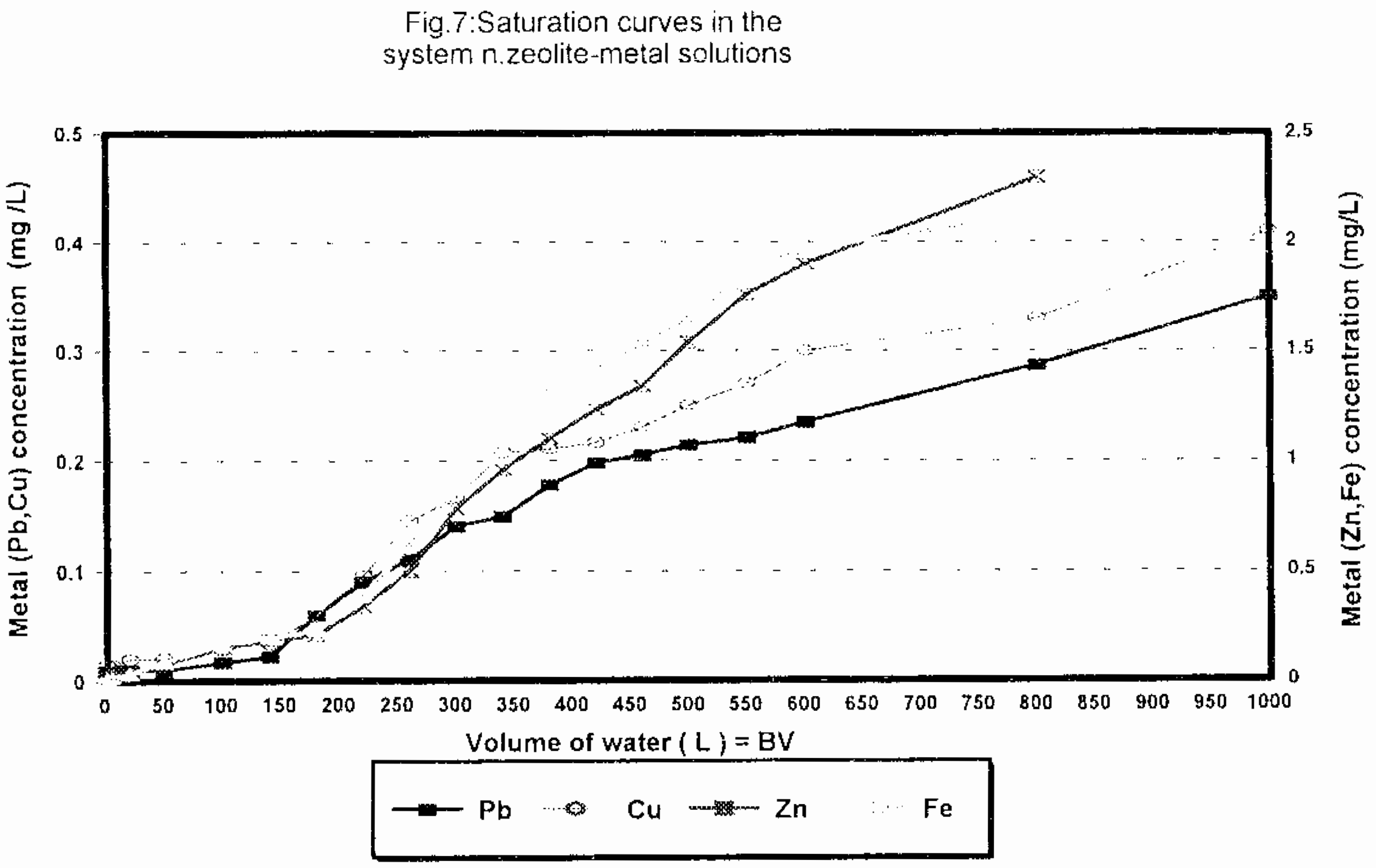

Fig 7: Saturation curves in the system of natural zeolite - solutions of Pb, Cu, Fe and Zn

On the basis of values of individual metals in effluents after passing through the sorption zone, the following may be established:

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- independent of the type of metal in the two-phase system of natural zeolite - solutions of metals Pb, Cu, Zn and Fe, the metal content is within the limits of trace detection up to $V_{effluent}$ = BV = 80 l.
- for Pb, the breakthrough point BC = $0.05c_0$ = 0.05 mg Pb/l was attained at V ~ 160 l, for Cu at V ~ 140 l (BC = 0.05 mg Cu/l) and for Fe and Zn at ~ 110 - 120 l of effluent with an input metal concentration of 4 mg/l (BC = 0.2 mg/l).
- the maximum effluent volume which still allows for faultless discharge (MAC = 2mg/l) into the recipient was in the case of Zn and Fe solutions with c_0 = 4 mg/l approximately 600 l and for Cu solution (MAC = 0.5 mg/l) with c_0 = 1mg/l approximately 1200 l. Due to the well-known and experimentally proven high affinity of natural zeolite towards lead ions, the estimated maximum volume for Pb solution is within the range of $V_{effluent}$ ~ 1400 l – 1600 l at selected flow rates and column sizes.

Testing of continuous passive purification of synthetic metal solutions and wastewater in a model laboratory device

A comparison of results and the determination of optimal conditions for attaining neutralization with recrystalized limestone and the sorption of metals on natural zeolite served as a basis for the dimensioning and construction of a model laboratory device (Fig. 8). The first phase included the simulation of continuous purification of synthetic metal solutions. In the second phase – the purification of wastewater from an abandoned mine Sitarjevec of Pb - Zn - Ba ores – the effectiveness of the selected procedure was confirmed.

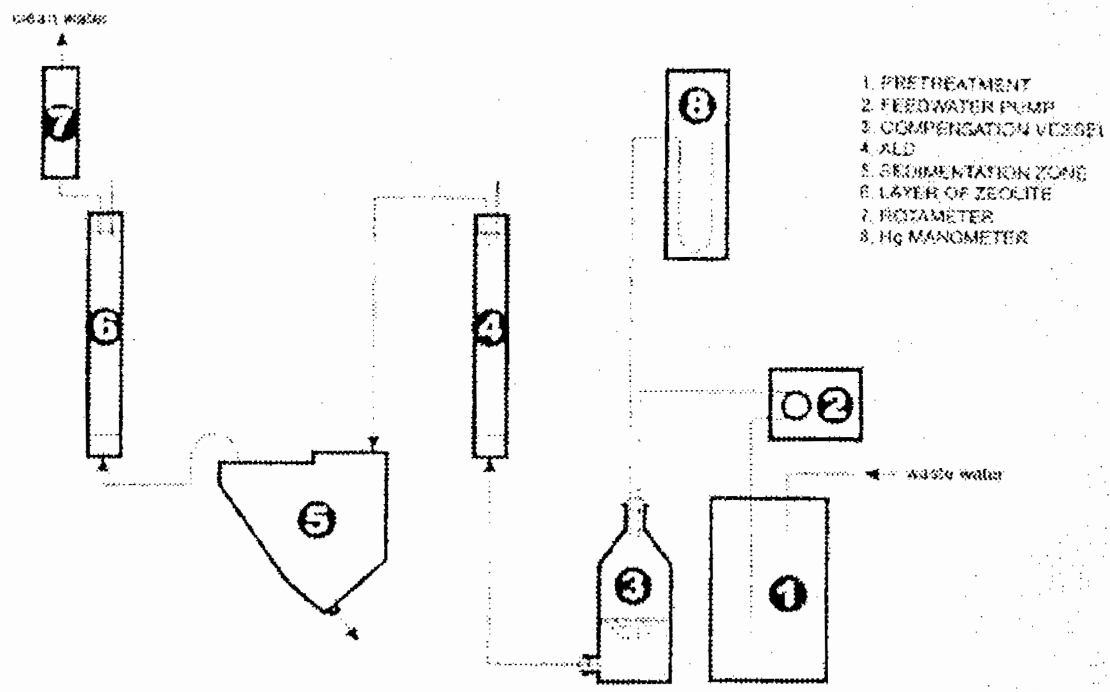

Fig. 8: Schematic presentation of the model laboratory device for the passive purification of water contaminated with metal ions

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The efficiency of processes employed in passive purification procedures depends on the chemism and kinetics of reactions in the systems. Compared to conventional procedures, the reactions progress at lower rates, which is why the residence times prior to discharge from the system must be long enough. In past years, many passive systems were dimensioned according to guidelines that were not based on the availability of land, the chemism and kinetics of reactions, but solely on the content of pollutants in influents and effluents. The new approach based on loading capacity (Hedin, et al., 1994) enables the more accurate estimation of the system's efficiency and the comparison of various passive systems differing in size, chemical composition of water and liquid flow rate through the system. As the biological zone of the passive procedure was not employed in our experiment, the equations for the calculation of carrying capacity had to be adapted to the operating conditions of our model laboratory device (neutralization - sedimentation - sorption). Comparative calculations have shown that equations of loading capacity may be successfully adapted by replacing the surface of marshes with the mass and specific surface area of materials used as sorbent in the column. On the basis of the loading capacity of the system, the rates of removal of individual components were calculated using the equations:

$$v = 1.44.k.\ \phi\ (Me_{input} - Me_{output})\ /\ P \qquad /1/$$

$$P = f(m, S_{mr}) \qquad /2/$$

where:
v - rate of removal
k - factor of the flow regularity
ϕ - flow of liquid through the system
Me - input or output concentration
P - parameter dependent on mass (m) and the specific surface (S_{mr}) of material used for pH regulation and sorption

Table 2 shows the calculated rates of removal of metals present in water solutions (Pb, Cu, Cd and Zn) at various levels of influent pollution (c_0 = 2 - 15 mg/l) and rates of liquid flow (2.4 - 6.0 $m^3/h.m^2$) through the system. The efficiency of the procedure - rates of removal of individual components - is calculated for BV = 50.

Table 2: Calculated rates (v_1,v_2) of removal of metals present in water synthetic solutions

		Pb	**Cu**	**Fe**	**Zn**
c_0= mg Me^{2+}/l		**2.0**	**2.0**	**2.0**	**2.0**
Φ=2.4 $m^3/h.m^2$	v_1 (g/m^2.day)	1.99	1.81	1.39	1.31
Φ=6.0 $m^3/h.m^2$	v_2 (g/m^2.day)	3.20	3.08	2.91	2.99
c_0= mg Me^{2+}/l		**5.0**	**5.0**	**5.0**	**5.0**
Φ=2.4 $m^3/h.m^2$	v_1 (g/m^2.day)	4.02	3.39	3.12	3.31
Φ=6.0 $m^3/h.m^2$	v_2 (g/m^2.day)	8.52	7.65	7.54	7.99
c_0= mg Me^{2+}/l		**10.0**	**10.0**	**10.0**	**10.0**
Φ=2.4 $m^3/h.m^2$	v_1 (g/m^2.day)	8.05	6.77	6.32	7.65
Φ=6.0 $m^3/h.m^2$	v_2 (g/m^2.day)	17.20	16.1	15.7	15.8
c_0= mg Me^{2+}/l		**15.0**	**15.0**	**15.0**	**15.0**
Φ=2.4 $m^3/h.m^2$	v_1 (g/m^2.day)	12.75	11.99	8.88	11.24
Φ=6.0 $m^3/h.m^2$	v_2 (g/m^2.day)	25.20	23.85	20.95	23.09

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According to a series of analyses of mine water in the winter-summer period, the average Fe_{tot} and zinc concentrations in mine water from Sitarjevec are 14 mg/l and 5.5 mg/l, respectively. In the first phase, the tests were conducted at a flow rate of 6 $m^3/h.m^2$, corresponding to the top limit of the selected flow rate range, and then repeated at a flow rate of 2.4 $m^3/h.m^2$.

Figures 9 and 10 show the attained rates of removal of Fe and Zn from mining wastewater and synthetic metal solutions.

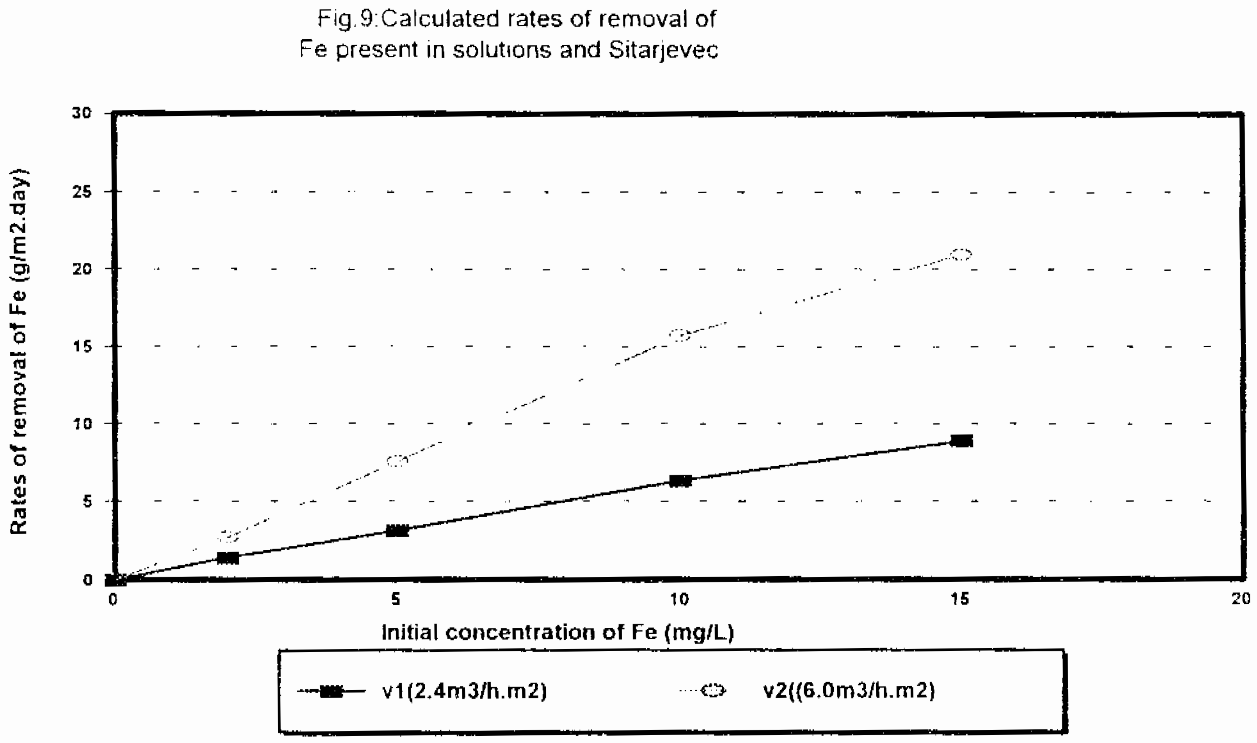

Fig. 9: Comparison of rates of removal of Fe from synthetic solutions and mining wastewater achieved in the model laboratory device

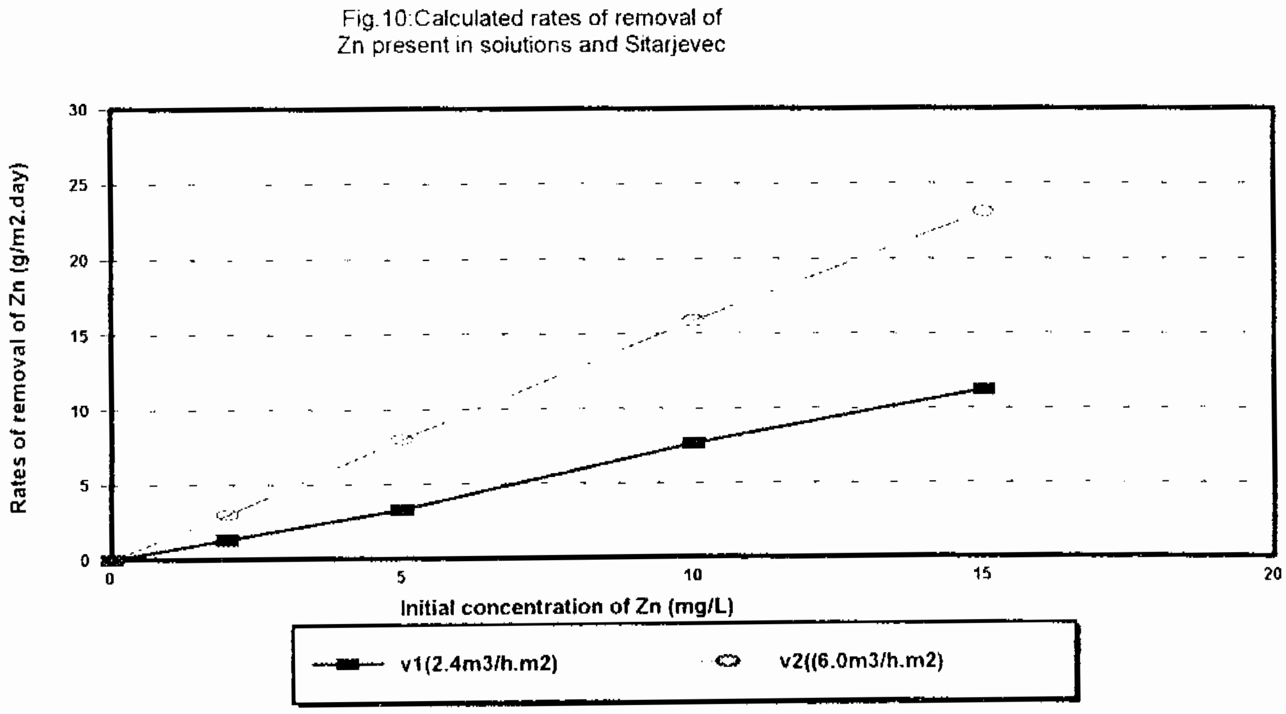

Fig. 10: Comparison of rates of removal of Zn from synthetic solutions and mining wastewater achieved in the model laboratory device

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On the basis of the obtained results and calculated rates, the following may be established:

- the wastewater flowing from the mine shaft contains 14 mgFe_{tot}/l and 5.5 mg Zn/l, while Pb, Cu and Ag appear in traces. Sulfate content is within admissible limits for discharge into a recipient.Due to the pH value of wastewater, part of the iron is present in precipitated form. By the addition of a reservoir before the ALD phase, Fe content may be reduced by approx. 50% and Zn content by approx. 40%. Thus, the water composition before entry into the ALD layer is brought the limits of standards for the utilization of ALD in the passive system.
- because of Fe's coagulation properties, approx. 30% of Fe and approx. 40% of Zn present in the liquid are, at the attained pH (7.5 - 7.8) and residence time of 24 hours, removed in the sedimentation zone which follows ALD, without the addition of polyelectrolytes.
- the iron and zinc content in the water entering the natural sorbent zone is within the range of MAC for discharge into the recipient. The role of a natural zeolite is to reduce the content of present metals to traces.
- the attained rates of removal of iron and zinc from mine water are within the ranges of rates achieved in the case of passive purification of synthetic metal solutions.

CONCLUSION

The results of chemical analyses of selected samples of actual mining wastewater in Slovenia have confirmed the suspected increased content of metal ions in mining wastewater, depending on the mineralogical composition of individual ore deposits. Despite the proven pollution of the environment - water currents and accumulations receiving mine leachate and wastewater, adequate procedures (conventional or alternative) for reducing the content of toxic components were not introduced or at least investigated in any of the cases discussed.

For the purification of acid wastewaters of mostly abandoned and still existing mines, the so-called passive purification methods were introduced in other countries. These include the pH regulation phase combined with the zone of biological decomposition in a natural or artificial marsh and/or sedimentation zone. Because limestone rocks are predominant in Slovenia, typical acid wastewaters do not appear, which is why the direct adoption of the pH regulation - precipitation - biological decomposition process can not be considered an ideal solution to this problem.

The aim of experimental studies of passive methods adapted to Slovenian climatic conditions (presedimentation - pH regulation - sedimentation - sorption) and the derivation of equations of loading capacity of the designed model device for passive purification was to confirm the suitability of these procedures for their successful application in Slovenia. Nonmetal minerals from exploited Slovene deposits were used: calcite for the regulation of pH value and zeolite tuff for the sorption of present metal ions. The derived equations based on the loading capacity of the system enable the calculation of rates of removal of

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individual components present (g/m^2.day) in the influent, as well as an evaluation of the effectiveness of selected methods as regards the size of systems and the level and type of pollution. The results of our model laboratory system are comparable with those of conventional passive purification systems, which employ, in addition to the studied phases, also biological decomposition.

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