Comparison of Al samples from electrolysis production and elemental Al from colloids

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Porovnanie vzorky Al vyrobeného elektrolýzou a elementárneho Al z koloidov

Sediments of specific composition and content of precipitates were found as a consequence of increased concentration of sulphate at the Quaternary groundwater. Precipitates with elemental Al^0 and fibres of alloy of Si^0, Fe^0 and Al^0 (max size of Al^0 spots cca 300x100 microns) from colloids of $Al_2O_3.nH_2O$ from borewells at Podluží were identified by RTG analyses and SEM in more then 20 analyses. Structure of colloids of $Al_2O_3.nH_2O$ was verified by ^{27}Al MAS NMR from several VIS borewells:A comparison of chemical composition of Al samples produced by electrolysis at Slovalco Ltd. Co. and of elemental Al^0 revealed some parallel in composition and their appearance. Samples ŽIAR1 and ŽIAR3 have similar chemical composition of Al with Al from VIS 15 but they differ in appearance. The rest of group (samples ŽIAR 2, ŽIAR 4, ŽIAR 5) differs from VIS 15 in composition and appearance of basic Al matter and specific alloys of Al, Si, and Fe.

Key words*: Sulphate, sediments, Fe minerals, elemental Al^0 and Si^0, SEM analysis of Al from colloids and from electrolysis*

Introduction

The amount of sulphate in wellfields at the Quaternary groundwater of the Morava river watershed increased for 37 years occassionally to the concentration of 300-400 mg/l of sulphate, as it was in 1997 at Kněžpole, while 60 l/s of drinking water were exploited (Ďurďová 2002). The process caused by many factors of natural conditions of the area and by the involvement of anthropogenic activities is accompanied by the occurrence of sediments and sludges of thickness of 2,0-4,0 m in the indicating system of borewells VIS 1-VIS 21 in the wellfield Podluží, Southern Moravia, Czech Republic (Ďurďová 2004). Sediments, which have been formed within last 15 years, contain white hydrophilic colloids (composed of 49,6 % of Al_2O_3. nH_2O with the appearance of white flocks floating in water), black sludge of hydrophobic colloids rich in water (composed of Fe, Mn, Al, and S, in some cases having the composition of pyrite), red-brown sediments in which were verified by RTG minerals of Fe: goethite, magnetite, lepidocrocite, pyrite, greygite (Ďurďová 2005).

In the sludge composition there is a predominance (in majority of cases) of Al_2O_3 as a result of the process of aluminisation when clay minerals are dissolved by sulphates. This was confirmed by the presence of Al stalactites in the sludge of borewells (Ďurďová 2005). The extreme oxic-anoxic conditions caused by the occurrence of H_2S in the sediments of borewells, together with the used technical equipment of borewells with Fe cases in combination with VUGI filters (perforated cages formed as a net of polypropylen) with little stripes of Al strongly contributed to this process of aluminisation. The mentioned sulphate concentration and the conditions at borewells resulted in the formation of a layer of sediments, 2,0 - 4,0 m thick.

As to the formation of Al and Si rich oxides and oxyhydrooxides in the samples, the reaction of water with aluminum and its alloys has been of concern to corrosion chemists since the commercial use of the metal. The passive aluminium (i.e. metal protected by a continuous oxide film) is practically stable in even boiling water. Aluminum which has been depassivated by a slight amalgamation of its surface, vigorously reacts with cold water or moist air until the metal is consumed. In the temperature range of 20-80°C, an increase in the mass of surface film follows exponential time laws after an induction period, whose duration is inversely proportional to temperature. Hart (1957) was seemingly the first who found that the films formed between 20-80°C are layered with an amorphous layer near the metal interface is followed by the one consisting of gelatinous boehmite and bayerite or well crystallysed boehmite grown on the outer surface. The ratio of the three strata changes with the temperature, pH and the time of exposure. When formed at the room temperature, the films may be made up of only two optically distinguishable layers, both of them consisting of X-ray indifferent (“amorphous”) material (Wefers K., 1961). The conditions of Al solubility in water (outside neutral pH, i. e. at lower and higher pHs) are well known.

In our case there is also the Fe concentration from water and cages. We list a few details about the solubility of Al under the normal temperature and pressure:

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- in the presence of Fe^{2+} Al is soluble at the concentration of 10^{-5} mol/l at pH below 5,5 and above 10,5; at the concentration 10^{-3} mol/l at pH below 4,0 and above 13,0;
- in the presence of Fe^{3+} is Al soluble at the concentration of 10^{-5} mol/l at pH below 5,5 and above 9,0; at the concentration 10^{-2} mol/l at pH below 4,0 and above 13,0 (Valeton I., 1966)

From this can be concluded that oxidised forms of iron increase the Al solubility, which is related to the Fe cages in borewells which are well corroded after 15 years. From the newest research results presented at congresses (e.g. Acid Rain Prague 2005) it is obvious that the generation of Al colloids is possible even under mildly acidic conditions (pH 5,0 –6,5, which could be at wall of the Fe cages) if water is mixed with a different load of protons and metals. This mixing favour the generation of colloids by hydrolysis of iron (Fe) and aluminium or by dissolution of clay minerals and the precipitation of secondary ferric oxides (Ulrich K.U. et al. 2005).

The acidification of soils and surface waters increases the mobilization of Al but there are some new findings on this dynamics. Aluminium fluxes and dynamics in streams were verified in some cases as more related to natural processes and types of soil than to S-depositions, indicating the catchment specific condition (total organic carbon, pH) to be of a greater importance for the Al chemistry (Löfgren S., Hultberg H. 2005). Our research results prove that these facts are well applicable to groundwater systems.

Investigation of colloids, precipitates and elemental metals

In white colloids predominantly composed of $Al_2O_3.nH_2O$, there is Al_2O_3 at the content of 49,6 weight %, SiO_2 (3,4), Fe_2O_3 and CaO (0,701 and 0,773, respectively), the rest is bellow 0,1 %: Na_2O (0,1), MnO (0,035), K_2O (0,039), MgO (0,036), TiO_2 (0,007), P_2O_5 (<0,005) and some metal precipitates pieces. Precipitates are of usual size, i.e. 0,5 cm x 0,9 cm, containing spots of elemental Al^0 (maximum length of size, ca. 300x100 microns, usually 10-30 microns wide) with thin fragile fibres of alloy of Si^0, Fe^0 and Al^0 being inserted inside were confirmed by the RTG and SEM analyses. As in the borewells cages were used stripes of Al, which could be the source of alumogels formation, the composition of Al alumogels was verified by the ^{27}Al MAS NMR (Magic Angle Spin, Nuclear Magnetic Resonance) spectroscopy of 6 samples from the borewells VIS. It was revealed, that the Al alumogels are not from one single (artificial) source (Al stripes). The Al alumogel especially from the VIS 2 contain colloids having distinct $Al(O)_4$ centers, which are similar to the ε – Keggin polyoxocation $AlO_4\ Al_{12}(OH)_{24}\ (H_2O)_{12}^{7+}$ (aq) $[Al_{13}]$ formed via the aggregation of the Al_{13} nanoclusters (Furrer et al. 2002). They were previously found by other authors (e.g. Furrer et al. 2002, Kai-Uwe Ulrich et al.2005 in Germany and California). In the case of borewells from Podluži, the sorption of many ions may be expected including little metal precipitates with the elemental Al^0 in a micron scale.

Comparison of samples of Al from colloids and the electrolysis

In borewells we found alumogels with spots of elemental Al under specific conditions (high concentration of H_2S) and so we compared them with several kinds of Al from the regular technical electrolytic production. This publication presents a comparison of samples of elemental Al^0 found in borewells at $Al_2O_3.nH_2O$ colloids and samples of Al prepared especially for our research purpose at the Slovalco Ltd. Co., at ŽIAR nad Hronom, Slovak Republic. The samples were prepared by Ing. Jozef Lovčičan according to the chemical composition of elemental Al^0, whose pieces were found in white colloids of $Al_2O_3.nH_2O$ at VIS 18 at Podluži). The composition was repeatedly verified by the microprobe analysis in 2004 and 2005 at the Institute of Geological Sciences, Masaryk Univerzity Brno by RNDr.P.Sulovský. The analysis of samples from the Slovalco Ltd. Co., and from the VIS 15 was made at the State Geological Institute D.Štůra in Bratislava by RNDr.I.Holický in 2005.

The industrial production of aluminium consist of two steps. Al_2O_3 is produced from bauxite in chemical way and from this oxide (in electrolyzers with the use of cryolite) aluminium is gained by electrolysis having 99,3 – 99,6 % of Al. The point of melting of aluminium is 659 °C, the point of melting of Si is 1415 °C, and the point of melting of Al_2O_3 is 2000 °C. All these facts are extremely important as to appearance of studied samples of Al and the shapes of Si crystals and other segregates from the Slovalco Ltd. Co. The chemical composition of the alloy of Al with another metals is given by norms: e.g. Al for the general technical use is according to the Czech Technical Norm ČSN 42 4385 (alloy $AlSi_20Cu_2NiMgMn$) composed of (in weight %): Si (19,00-22,00), Cu (81,50-2,00), Ni (0,50-1,00), Mg (0,10 – 0,40), Fe (max. 0,50), Ti (max. 0,15), Zn (max. 0,10) and additions (max. 0,75). This type of Al could be used in Al strips of borewells. The very low content of Fe, which is not added to Al in the production process can be an indication of a level of the involvement of some natural processes not related to the electrolysis.

Common features of the samples of Al from colloids and the electrolysis

Samples of Al from the alumogels of the VIS 15 and from the electrolysis have some common features only in the cases of samples ŽIAR 1 and ŽIAR 3 but there are many exceptions showing a complicated situation. The samples ŽIAR 1 and ŽIAR 3 are the nearest to each other by the appearance and by the chemical composition as given in Tab. 1 under numbers 51970 and 51946, (as they were referred to by the laboratory of the Slovalco Ltd. Co.). Our results of the chemical composition of the average sample and the separate points are listed below.

Average Al composition

The appearance of samples ŽIAR 1 a ŽIAR 3 is very simple as it includes, besides monolithic background light grey colour of Al (nevertheless darker slightly than in the elemental Al from VIS 15), some glittering fibers. In the sample ŽIAR 1 the average Al composition is counted from the points 2, 3, 5 and 6 and is (in weight %): Al (96,51), both Si and Mg (0,35), Fe (0,13), and metallic glittering fibers (organized into lines as if they were forming a boundary of some cells) have in the sample ŽIAR 1, point 4, the composition of alloy in weight %: Al (75,05), Fe (18,99) and Si (0,12).

Tab. 1. Chemical composition of samples ŽIAR 1, ŽIAR 3, ŽIAR 2, ŽIAR 4, ŽIAR 5 produced by electrolysis at SLOVALCO, Ltd. Co., ŽIAR nad Hronom and the chemical composition of samples Average ŽIAR 1, ŽIAR 3, ŽIAR 2, ŽIAR 4, from the SEM analyses at GÚDŠ Bratislava. Data in weight %.

Element	Sample					Average			
Sample number	ŽIAR 1 51970	ŽIAR 3 51946	ŽIAR 2 S-035	ŽIAR 4 51965	ŽIAR 5 51911	ŽIAR 1	ŽIAR 2	ŽIAR 3	ŽIAR 4
Al	98,888	99,727	80,104	89,004	91,755	96,5123	85,8998	94,0482	95,1653
Si	0,451	0,057	19,40	9,46	9,70	0,35856	12,1536	0,1192	1,2609
Mg	0,383	0,002	0,048	0,403	0,395	0,35124	0,0347	0,0003	0,2912
Fe	0,229	0,203	0,260	0,084	0,076	0,13538	0,3399	3,3922	0,0103
Mn	0,038	0,002	0,083	0,016	0,046	0,01918	0,1061	0,0124	0,0378
Zn	0,003	0,009	0,026	0,005	0,008	0,05328	0,0362	0,0217	0,0030
Cr	0,001	0,001	0,003	0,0000	0,001	0,01508	0,0000	0,0067	0,0097
Ni	0,003	0,003	0,006	0,003	0,003	0,04034	0,0243	0,0478	0,0099
Cu	0,0004	0,0004	0,0125	0,9883	0,0003	0,01952	0,0631	0,0068	0,5691
Ti	0,009	0,006	0,027	0,040	0,115	0,00318	0,0340	0,0184	0,0645
Pb	0,001	0,001	0,002	0,000	0,001	0,00384	0,0342	0,0033	0,0434
Sn	0,000	0,0000	0,001	0,000	0,001	0,00456	0,0159	0,0033	0,0000
Total	100,00	100,00	100,00	100,00	100,00	97,5510	98,6609	96,7104	97,4680

Explanation of Tab. 1: The samples ŽIAR 1- ŽIAR 5 are listed according to the similarity in the order 1, 3, 2, 4, 5. The composition of samples named Average ŽIAR are from the SEM analyses (SEM at GUDS Bratislava, Slovakia): average ŽIAR 1 from points 1, 2, 3, 5, 6; average ŽIAR 2 from points 10, 11, 14; average ŽIAR 3 from points 7, 8, 9; average ŽIAR 4 from points 20, 21; samples ŽIAR 5 are not average as they are from listed points 24, 26, 22.

In the sample ŽIAR 3, the Al average composition at the points 7, 8, 9 is (in weight %): Al (94,048), Si (0,12), Mg (0,0003), Fe (3,39). Elemental Al from colloids of VIS 15 has two shades of grey colour darker and lighter, which differ in their composition. Elemental Al of the darker phase from VIS 15 has a composition (average from the points 28 and 30, in weight %): Al (96,37), Si (only 0,51), and Fe (0,047-0,097). Elemental Al of the lighter grey phase is richer in Si (at point 29, in weight %): Si (23,31) and Al (75,76).

The composition of elemental Al from VIS 15 is near to those of samples of Al from the electrolytic production ZIAR 1 (point 1- 96,74 %, point 2 %, point 3 – 96,78, point 4 - 95,49 %) and ZIAR 3 (point 7-97,2 %, point 9 -95,86 %).

The elemental Al from the sediments (mud with colloids) of VIS 15 from the points 42, 43 and 35 has a composition 95,25-96,27 % of Al and 0,470 – 0,497 % of Si, with a similar low concentration of Mn and Fe and some resting metals in traces (Cu, Zn). It was found in the nature during the verification of alumogels.

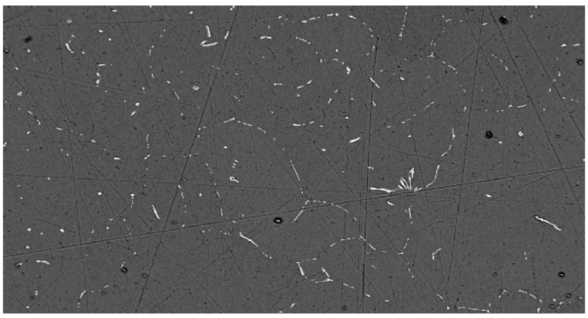

Fig. 1. ŽIAR 1- Sample of Al from at electrolysis production at SLOVALCO, Ltd. Co. at ŽIAR nad Hronom. Chemical composition of surveyed sample: dark grey colour is Al (weight %): Al 96,7 - 96,83, Si 0,34-0,43, total sum of metals is 96,9-97,76. Chemical composition of surveyd samples is from analytic. points 1-6.

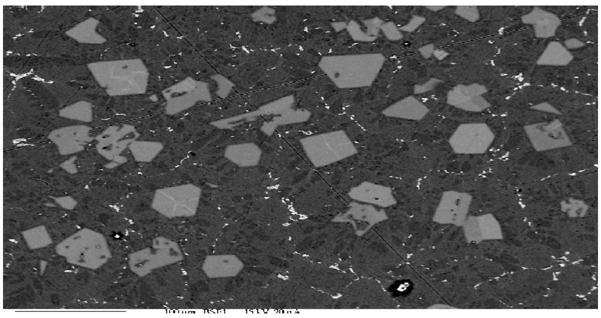

Fig 2. ŽIAR 2- Sample of Al from at electrolysis production at SLOVALCO, Ltd. Co. at ŽIAR nad Hronom. Composition (in weight %): Darker Al basic mass is 94,95 of Al and Si 1,64. Lighter Al basic mass is 79,92 of Al and 18,8 of Si.

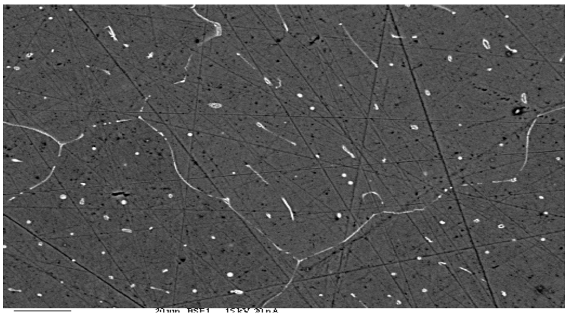

Fig 3. ZIAR 3- Sample from electrolysis production at SLOVALCO, Ltd. Co. at ŽIAR nad Hronom. Composition (in weight %) as was given by producing company: Al 99,727, Fe 0,203, Si 0,057. Composition of basic Al mater (in weight %) from our analysis: Al 97,20, Si 0,0, Fe 0,2343. White fibers were not so far anaylsed.

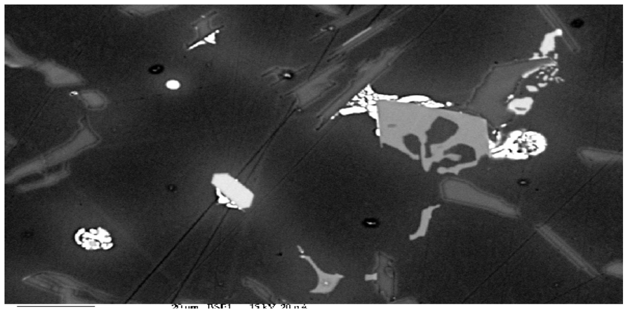

Fig 4. ŽIAR 4- Sample from electrolysis production at SLOVALCO, Ltd. Co. at ŽIAR nad Hronom. Composition (in weight %): Basic Al matter average composition (from points 20 and 21) is: Al 95,16, Si 1,26, Mg 0,31, Cu 0,669, Fe 0,0207. The shape as head by centre of picture has composition (in weight %): Al 15,91, Si 29,66, Mg 33,69, Fe 0,0403, Cu 20,62, sum is 99,75.

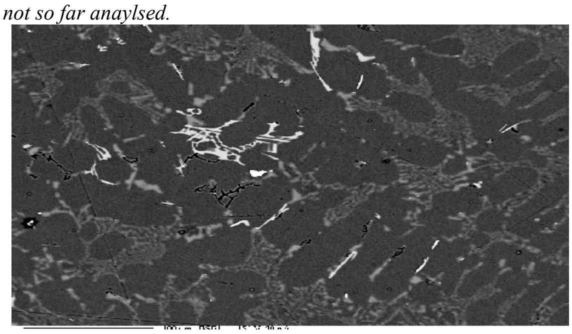

Fig 5. ŽIAR 5- Sample from at electrolysis production at SLOVALCO, Ltd. Co. at ŽIAR nad Hronom. Composition (in weight %): Al basic matter dark grey Al 95,18 and Si 1,3459. Islands of middle grey segregated Al matter have composition: Si 89,3521 and Al 4,9654.

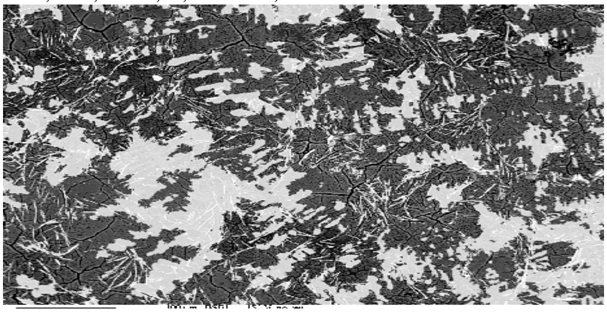

Fig 6. ŽIAR 6- Sample of Al from colloids from VIS 15 from Podluží. Basic matter (has middle grey colour with black ruptures) is consisting of oxides or hydrooxides of Si and Al (in weight %): Si 21,86, Al 14,37, Ca 1,04, S 0,48, sum is 37,95) there are present spots with elemental Al of light grey colour (96,74 weight %). The elemental Al is of 2 composition with lighter and darker grey colour: the lighter grey: Al 76,76 and Si 23,3 weight %, and the darker grey has Al 96,1 and Si 0,5 weight %. Through the whole space of basic matter and of elemental Al going go white fibers of alloy of elemental metals: Al^0, Si^0 and Fe^0 are in usual ratio in weight % : Al^0 44: Si^0 25,4: Fe^0 23,6.

Fibers and their genesis in samples from Slovalco, Ltd.Co

Metallic fibers are another common feature of samples ŽIAR 1, ŽIAR 3, and VIS 15 although in the 3D space the fibers are probably plates. Actually there are some differences in these fibers, too. In case of VIS 15, the fibers are almost equally widespread in the sample in parts of basic matter and also in spots of elemental Al (Al has 96,37 %).

The basic matter of sample VIS 15 is (according to the analysis at two points) a mixture of Al and Si oxides whose total sum is about 40 weight %, the rest is water. According to the analysis of VIS 18, there is a composition similar to $FeSO_4$.n H_2O.

Fibers go crossing edges from the basic matter of sample to the elemental Al^0 part as their length is from a few microns to 15 microns, often about 10 microns wide and orientation to all directions. Another difference is that the occurrence of fibers which is higher in VIS 15 than in ŽIAR 1 and ŽIAR 3. The fibers shape at VIS 15 (as well as VIS 18) is straight like short needles on the desk joining each other and less crossing, some are broken. They never form continual oblique long lines as it is in case of fibers of ŽIAR 1 and ŽIAR 3 samples, for which we found a very adequate parallel with samples of cells of anodic oxide in articles focused on oxides and hydrooxides of aluminium and metallurgic processes of Al electrolysis (K. Wefers, Ch. Misra, 1987) from the description of some aspects of the starting electrolytic production, we found how the features of the "cell appearance"of samples ŽIAR 1 and ŽIAR 3" were aformed:

In the first few seconds of anodic polarisation, a barrier layer grows as it does in a non-solvent electrolyte. Appearing first at areas of high free energy such as subgrain boundaries, the cells rapidly cover the electrode surface, attaining a polygonal, ideally hexagonal cross section as they fill the available space. Once the cell pattern has been established it remains unchanged while the oxide continues to grow. The length of cell may reach more than 100 µm. The diameter is a function of the voltage and electrolytic composition (K. Wefers, Ch. Misra, 1987).

Tab. 2. Chemical composition of samples ŽIAR 1, ŽIAR 4, ŽIAR 5- produced from electrolysis production at SLOVALCO Ltd. Co. at ŽIAR nad Hronom and from VIS 15 from Al colloids from Podluží. Data in weight %. N.i. - not identified

SAMPLE/ Element	ŽIAR 5 Al point n. 24	ŽIAR 5 Al point n.26	ŽIAR 5 Si crystal point n.25	ŽIAR 4 CARO Point 15	ZIAR 1 Fiber Point n.4	VIS 15 Al without Si, Points 42, 43, 35, 28	VIS 15 Al with Si point 29	VIS 15 basic matter Al+Si oxid Point 31	VIS 15 Fiber Point 27
Al	95,1819	81,9813	4,9654	45,8321	75,0523	96,3765	75,7636	14,3755	44,4278
S	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	0,4829	n.i.
Ca	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	1,0432	n.i.
Si	1,3459	17,1598	89,3521	25,9812	6,3481	0,5104	23,3104	21,8663	25,4377
Mg	0,3734	0,7397	0,0334	15,8386	0,1724	0,0000	0,0000	0,0424	0,0069
Fe	0,0153	0,2891	0,0185	9,5838	18,9911	0,0973	0,0406	0,0465	23,6307
Mn	0,0084	0,1253	0,0158	0,4432	0,8055	0,0378	0,0480	0,0128	3,5050
Zn	0,0000	0,0542	0,0265	0,0996	0,0000	0,0000	0,0000	0,0000	0,0447
Cr	0,0074	0,0209	0,0000	0,0000	0,0000	0,0000	0,0185	0,0037	0,0078
Ni	0,0000	0,0124	0,0235	0,2154	0,1587	0,0000	0,0000	0,0179	0,0988
Cu	0,0340	0,0000	0,1114	1,2876	0,0283	0,0352	0,0000	0,0318	0,0000
Ti	0,2015	0,0793	0,0077	0,0000	0,0040	0,0061	0,0066	0,0000	0,0000
Pb	0,0000	0,0000	0,0031	0,0057	0,0000	0,0376	0,0769	0,0300	0,0496
Sn	0,0038	0,0154	0,0000	0,0024	0,0077	0,0000	0,0000	0,0000	0,0000
Total	97,1714	100,4773	94,5575	98,2896	101,5682	97,1010	99,2646	37,9529	97,2091

The samples ŽIAR 1 and ŽIAR 1 are examples of Al from the electrolysis production with a minimal addition of another metal elements (ŽIAR 1: Fe 0,229 %, Si 0,451 %, ŽIAR 3: Fe 0,057 %, Si 0,203 %) so we have caught even the cell structure from the anodic polarization and we can see their diameters.

Composition of fibers from samples is VIS 15 and ŽIAR 1 and ŽIAR 3:

The composition of fibers from VIS 15 (in weight %) : Al (44,4278), Si (25,4377), Fe (23,6307), Mn (3,5050), Zn (0,0447), Ni (0,0998). A similar fiber composition was found previously also at the same location at Podluží from VIS 18 (in weight %):

Point 6: Al (43,43), Si (28,86), Fe (23,04), Mn (3,44), S (0,07), Ca (0,07), total: 98,96.
Point 7: Al (48,93), Si (29,21), Fe (24,31), Mn (4,25), S (0,04), Ca (0,04), total: 106,77.
Point 8: Al (44,70), Si (27,34), Fe (23,36), Mn (3,78), S (0,09), Ca (0,05), total: 99,33.

From these results we can be conclud the fibers composition of Al in colloids: Al is forming about 45 % and Si plus Fe are together 50 %, plus 3-4 % Mn form together an alloy of elemental metals.

The composition of fibers from ŽIAR 1 was not available but an analysis of metallic glittering matter is very similar to the fibers (point 4) has the results (in weight %): Al (75,0523), Si (6,3481), Fe (18,9911), another elements have a low concentration: Mg (0,1724), Mn (0,8055), Ni (0,1587) and Zn, Cr, Pb (0). A similar case was with the fibers composition from ŽIAR 3 (point 8, in weight %): Al (89,0735), Si (only 0,2994), Fe (9,7421), Mn (0,0302), Ni (0,1435), Zn (0,0651), Cr (0,0177), Sn (0,0009), Pb (0,0648), Ti (0,0088), Mg (0,0000).

For the verification of a complex composition of sample ŽIAR 3, we made an analysis of the sample area of circle with the diameter of 50 μm with the following results (average composition in weight %): Al (95,8619), Si (0,0582), Fe (0,2002), Mn (0,0070), Mg, Zn, Ni, Cr, Cu (0,0000), Sn (0,0091), Pb (0,0347), and Ti (0,0084).

The main differences in fibers-like shapes from ŽIAR 1 and ŽIAR 3 are their shape and that they have a higher concentration of Al and a lower concentration of Si and Fe, while the analysis of fibers from alumogels of VIS 15 and VIS 18 are very similar: about 50 % of Al and 45 % of Fe and Si together.

Basic differences between samples of Al in colloids and from the electrolysis production (ŽIAR 4, ŽIAR 5 and ŽIAR 2)

The samples of Al from ŽIAR 2, ŽIAR 4 and ŽIAR 5 represent the most different cases of Al examples in comparison with Al of VIS 15. Their composition was stated by the production company Slovalco (in Tab. 1) and we have done a “ local ” verification of the composition to find a detailed composition (in scale of several electrons) of interesting parts of samples.

ŽIAR 2

At the appearance of the sample ŽIAR 2 (Fig. 2), the basic background grey colour is composed of two shades: the darker grey means Al with a low Si content (94,95 % of Al and only 1,6485 % of Si, the rest metals have a low concentration (in weight %): Ti (0,0573), Ni (0,0531), Fe (0,0474), Mn (0,0211). The lighter grey colour of basic background is related to Al with more Si (in weight % the average from points 10 and 14): Al (85,89), Si (12,15), Fe (0,3399) and Mn (0,1061)(Tab. 2 for more details). Very typical for these samples are light hexagonal crystals of Si. At the point 14, an average analysis of ŽIAR 2 by a bunch of electron rays was originally taken and the result well represents the background matter composition: the ratio of Al:Si is 79,92 :18,87 (in weight %). Glittering white irregular fibers (as hairs) were analysed with the result (weight %): Al (75,78), Si (15,18), Fe (12,6052), Mn (2,920). The analysis of typical light grey hexagonal crystal of Si revealed a composition 91,54 % Si and only 0,7578 % of Al. In the Al sample from VIS 15, there are not crystals of Si and in case of fibers their appearance is slimmer – only 1-3, 5 microns at maximum.

ŽIAR 4

The appearance of sample ŽIAR 4 is excelling from all Al examples from Slovalco Ltd.Co. (with the composition stated by its laboratory 89,0 % Al and 9,46 % of Si see in Tab. 1). The basic Al matter is dark grey with a plenty elegant segregation of different shapes and colours with a more apparent Cu concentration. The basic Al matter average composition (points 20 and 21) is (in weight %): Al (95,16), Si (1,26), Mg (0,31), Cu (0,669), Fe (0,0207) (Fig. 4).

There are the most often segregations of Si rich crystals, which are lighter than the basic Al matter and have elongated shapes with a darker edge line whose composition is (in weight %): Si (85,8030), Al (4,9124), Mg (0,0142), Cu (0,4519), while all Fe, Mn, and Zn are 0,0000. At the center of Fig. 4 is a bizarre indented crystal (like an ugly head) with a composition (in weight %): Al (45,8321), Si (25,9812), Mg (15,8386), Cu (1,2876), Fe (9,5838).

A well crystallised Mg-Si-Cu-Al rich crystal (18 microns long, 7 microns wide) situated just opposite to the "head" has a composition with a low ratio of Al and higher Mg and Cu than usual (in weight %): Al (15,91), Si (29,6652), Mg (33,3968), Cu (20,6203), Al (15,9129), Fe (0,0403). Some shapes formed as sea shells with (points 17 and 18) an average composition: Cu (52,3301) and Al (47,1434).

ŽIAR 5

The samples ŽIAR 5 and ŽIAR 4 are very different in Al from VIS 15 but they have some common features as a dark basic matter with many segregations which differ from fibers of VIS 15 by wider shapes and a higher content of Mn and Mg. ŽIAR 5 produced for us at Slovalco has the composition (in weight %): Al (91,7550), Si (9,70), Mg (0,395) and Fe and Mn (0,076) and (0,046), respectively.

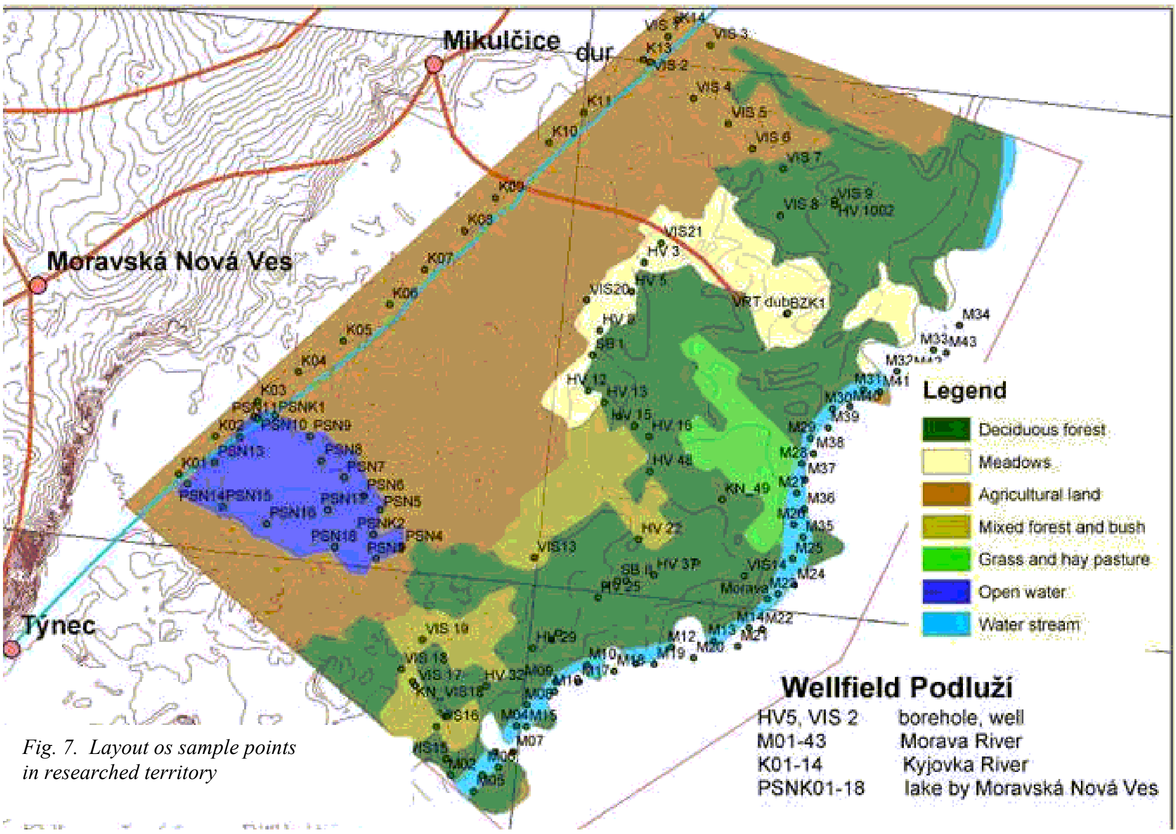

Fig. 7. Layout os sample points in researched territory

In Fig. 5 the Al basic matter is almost black or very dark grey (Al and Si in weight % are 95,18 and 1,3459, respectively) with islands of middle grey segregated Si matter of the composition (in weight %):

Si (89,3521) and Al (4,9654), respectively. In ŽIAR 4 and in ŽIAR 5 is a strong segregation of Si rich spots or islands in Al-rich basic space. In the picture (Fig. 5) there are metallic glittering shapes, especially a group of segregations of composition in weight %: Al (46,39), Si (25,99), Mg (14,9939), Fe (8,44), Mn (2,46) at the center. Another very bright segregation is at the center and has the composition (in weight %): Al (58,3604), Mn (17,7697), Fe (12,66), Si (9,7177), Mg (0,0000), Cr (0,2731). The average analysis area of the Al background (from about 50 microns) had a result (in weight %): Al (81,9813), Si (17,1598), Mg (0,7397), Fe (0,2891), Mn (0,1253).

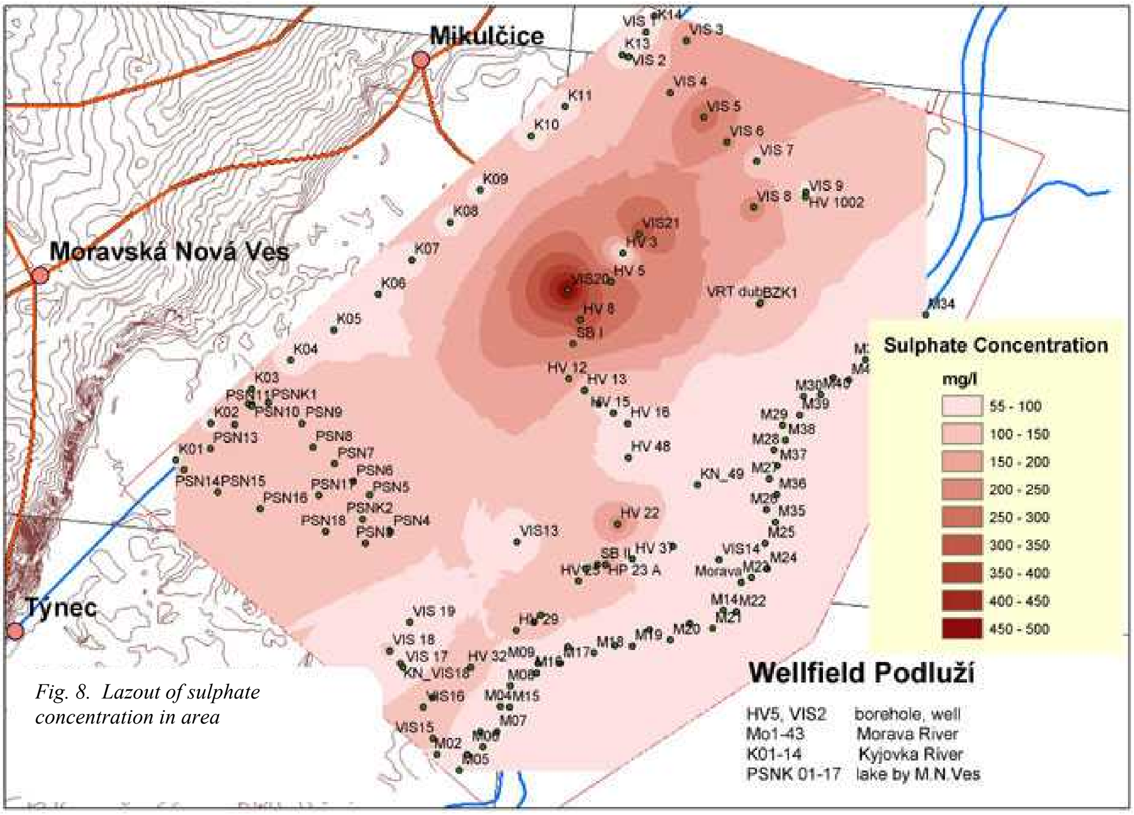

Fig. 8. Lazout of sulphate concentration in area

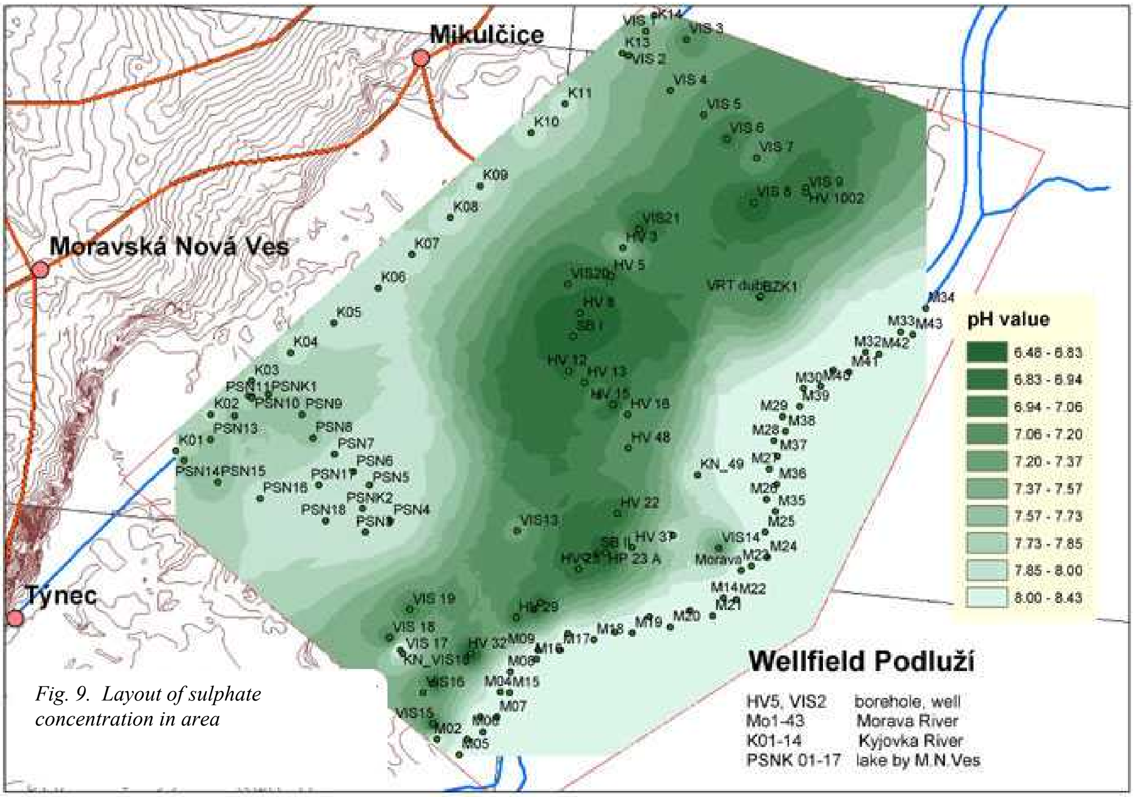

Fig. 9. Layout of sulphate concentration in area

Conclusions

The sediments with a specific composition and content of precipitates were found and surveyed as a consequence of increased concentration of sulphate at the Quaternary groundwater of Morava river watershed. From the monitoring borewells VIS, precipitates with Fe minerals and metallic pieces (cca 0,5 cm x 0,9cm) from colloids of $Al_2O_3.nH_2O$ with included islands of elemental Al^0 were identified by RTG analyses and by SEM in more then 20 analyses. Elemental Al^0 is occurring in a minimum scale: the maximum size of Al^0 spots is cca 300x100 microns and they were accompanied by fibres of alloy of Si^0, Fe^0 and Al^0. This article presents a comparison of samples of elemental Al from the electrolysis production at Slovalco Ltd. Co. (Slovak republic) and from alumogels from the VIS 15 borewell at Podluží (Czech Republic). The results showed that the samples ŽIAR 1 and ŽIAR 3 and the elemental Al^0 sample from VIS 15 have some common features in the appearance and composition but with many exceptions. Samples ŽIAR1 and ŽIAR3 have a similar chemical composition to Al from VIS 15 as they were produced to our dispositions, but they differ in the appearance of fibers and their composition.

Samples ŽIAR2, ŽIAR4, and ŽIAR5 have almost nothing in common with Al from VIS 15 and they differ in all ways. In samples ŽIAR2, ŽIAR4, ŽIAR5, the colour of basic background Al is darker there are many islands of Al segregations which are more rich in Si and another metals. In the basic Al matter of samples ŽIAR2, ŽIAR4, ŽIAR5 there are often striking bizarre forms of crystals and precipitates with an unusual metal alloys composition. The results of ^{27}Al MAS NMR spectroscopy of wet samples brought details on the structure and genesis of alumogels (from 6 borewells VIS) which act as sorbents for many metals and can mobilize them.

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