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Aluminium solubility in acid waters of the abandoned open pyrite mine at Wieściszowice (Rudawy Janowickie Mts., West Sudetes)

The study of chemical composition of waters in the abandoned open pyrite mine at Wieściszowice (the Rudawy Janowickie Mts., the W Sudetes, SW Poland) has been carried out with the aim of determining the conditions of mobilization and solubility of aluminium. Both the ion activities and the saturation of water samples with respect to mineral phases have been calculated using the WATEQ4F computer program. Sulphate waters have been found in the mine area, with total dissolved solids (TDS) in the range of 1500–5800 mg/l, low pH (2.50–2.98) and high concentration of aluminium, from $1.18 \cdot 10^{-3}$ to $6.52 \cdot 10^{-3}$ M (31.9–176 mg/l Al). The analysis of ion activities and chemical equilibrium of waters from the mine area indicates that aluminium solubility is controlled by the basic aluminium sulphate, $AlOHSO_4$. On the other hand, clay minerals (most likely kaolinite) control Al content in waters occurring in the outcrop of pyrite-bearing schists outside the mine area.

INTRODUCTION

In the Wieściszowice area in the Rudawy Janowickie Mts., a deposit of sericite-chlorite pyrite-bearing schists appears within the metamorphic rocks of the eastern cover of the granitoid Karkonosze massif. This pyrite deposit was exploited until 1925, and the pyrite itself was the raw material for the production of sulphuric acid. The three quarries and wide spoil banks with reworked schists have been left as evidence of old mining work.

Previous mineralogic studies of the pyrite-bearing schist deposit were devoted to the ore's paragenesis (S. Jaskulski, 1964; A. Piestrzyński, W. Salamon, 1977) as well as to the supergene sulphate minerals (J. Parafiniuk, 1991; J. Kubisz, 1964). The work of E. Balcerzak *et al.* (1992) dealt with an analysis of preliminary results of a hydrochemical study on the origin of composition of waters existing in the weathering zone of the deposit.

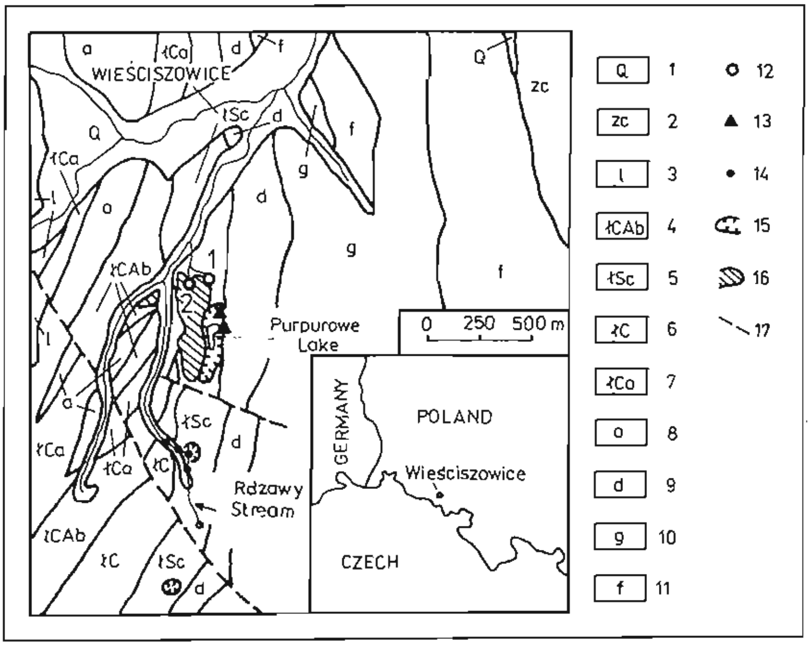

Fig. 1. Geological sketch of the studied area (after J. Szałamacha, 1956; J. Szałamacha, M. Szałamacha, 1988) and localization of the water sampling sites

1 — Quaternary deposits, 2 — Lower Carboniferous conglomerates, 3 — chlorite-albite schists, 4 — chlorite-albite-quartz schists, 5 — pyrite-bearing sericite-chlorite schists, 6 — chlorite schists, 7 — chlorite-carbonate schists, 8 — actinolite amphibolites and chlorite schists, 9 — diabases, 10 — gneisses, amphibolites and chlorite schists, 11 — phyllites, 12 — effluents (no. 1 and 2) in the spoil bank (sampled), 13 — effluents in the quarry (sampled), 14 — water sampling points in the Rdzawy Stream (after E. Balcerzak *et al.*, 1992), 15 — quarries, 16 — spoil banks, 17 — inferred faults

Szkic budowy geologicznej terenu badań (według J. Szałamachy, 1956; J. Szałamachy, M. Szałamachy, 1988) z lokalizacją miejsc opróbowania wód

1 — czwartorzęd, 2 — zlepieńce karbonu dolnego, 3 — łupki chlorytowo-albitowe, 4 — łupki chlorytowo-albitowo-kwarcowe, 5 — pirytonośne łupki serycytowo-chlorytowe, 6 — łupki chlorytowe, 7 — łupki chlorytowo-węglanowe, 8 — amfibolity aktynolitowe, 9 — diabazy, 10 — gnejsy, amfibolity i łupki chlorytowe, 11 — fyllity, 12 — wycieki (nr 1 i 2) na hałdzie (opróbowane), 13 — wycieki w kamieniołomie (opróbowane), 14 — miejsca opróbowania wód Potoku Rdzawego (według E. Balcerzaka i in., 1992), 15 — kamieniołomy, 16 — hałdy, 17 — uskoki przypuszczalne

The oxidation of pyrite leads (among other effects) to the increase of acidity in both surface and groundwaters along with the release to these waters of a number of chemical elements (including aluminium) that are mobile in an acid environment. The toxicity of dissolved aluminium to many animal and plant species is one of the main consequences of environmental acidification due to acid rain. Within the oxidation zones of the sulphide deposits, such acidification is locally taking place at a more intensive rate than that occurring in areas subjected to the effects of atmospheric pollution. In the area of the abandoned open pyrite mine at Wieściszowice, both the surface and groundwaters were found to have low pH and very high concentrations of aluminium.

The purpose of this paper is a presentation of an analysis of both the solubility and the mobilization of aluminium in the acid sulphate waters in the area of the abandoned open pyrite mine based on a new, comprehensive hydrochemical study.

METHODOLOGY AND REFERENCES

In 1991–1992, surface water in the Purpurowe Lake (Purpurowe Jeziorko), in the north, largest quarry, was sampled several times; effluents in the quarry and the spoil banks were dealt with in the same way. Figure 1 shows the places where water samples were collected. Water in the Pupurowe Lake was sampled twice (in July, 1991 and February, 1992) in several vertical profiles at each 0.5 or 1 m depth interval.

The components' assemblage in the water was determined with the aim of finding a genetic connection with the bedrock. A total of 41 water samples were analysed. Sulphates and chlorides were determined with the use of conventional titration methods, while fluorides were determined by the potentiometric method and phosphates by the colorimetric molybdate method. FAAS and ICP methods were employed to determine aluminium and remaining components.

The WATEQ4F computer program was used to calculate the ion and molecular activities and saturation with respect to mineral phases (J. W. Ball *et al.*, 1987). For water in Purpurowe Lake the average values were determined for each particular sampling depth interval. In this paper reference is also made to some previous water analyses (E. Balcerzak *et al.*, 1992). Localities of that previous sampling are also shown on Figure 1.

PETROGRAPHIC AND MINERALOGIC CHARACTERISTICS OF THE PYRITE DEPOSIT

The sericite-chlorite pyritic schists are part of the Leszczyniec Volcanic Formation (J. H. Teisseyre, 1973), in which quartz and quartz-chlorite schists are dominant. There is a strongly folded deposit series within the schists. It outcrops along meridian extent; length of the outcrop is about 4 km and its width is about 200 m. Different petrographic varieties were distinguished within the crystalline schists of this deposit (S. Jaskulski, 1964). They make up the following three distinct rock series: a superstratum, a mineralized zone, and an underlayers.

The superstratum is composed of chlorite and quartz-chlorite schists. The essential mass of the rock is made up of quartz granoblasts surrounded by chlorite plates. Of frequent occurrence are lenses and nests of calcite. The schists also contain a trace impregnation of fine dispersive pyrite grains and a dusty tuffogenic substance; laminae of albite are also present.

The mineralized zone proper is made up of sericite-chlorite schists impregnated with pyrite. The pyrite crystalloblasts, 1–5 mm in size, are surrounded by a mass composed of chlorite and quartz. The chlorite has been subjected to sericitization; in particular, this deals with the zones of strong mineralization. Laminae of tuffogenic material are also present. The pyrite contents of the deposit are variable, from a fraction of a percent to 70% by weight. Average contents in the deposit are in the range of 2.4–20.1% by weight (R. Nielubowicz, 1954; E. Błocki, 1955). Pyrite is accompanied with small amount of galena, sphalerite, and chalcopyrite. Quartz mineralization is common in the ore body. Metallization with Fe, Cu, Zn, and Pb sulphides was found in one of the types of quartz vein along with antimony sulphosalts of Cu and Pb (A. Piestrzyński, W. Salamon, 1977).

The underlayers represents a group of rocks of cataclastic character. The group contains aphanitic chlorite schists with calcite. There are also quartz and feldspar grains included in the rock matrix composed of chlorite, muscovite, quartz, epidote, pyrite, and iron oxides.

Both the detrital components of schists (quartz, sericite, chlorite) as well as illite with kaolinite and goethite (E. Balcerzak *et al.*, 1992) were found amongst the weathering products of pyrite-bearing schists. There is a rich supergene paragenesis of sulphate minerals in the area of the abandoned mine. It is made up of gypsum, copiapite, pickeringite, fibroferrite, slavikite, alunogen, and epsomite (J. Parafiniuk, 1991).

SOLUBILITY OF ALUMINIUM

Concentration of aluminium in natural waters is commonly in the range of 10^{-3}–10^{-8} M. The pH value appears to be a main factor which governs the mobilization of aluminium. However, its effect is to some extent modified by processes such as: equilibrium of solubility products with minerals, cation exchange, or formation of soluble complexes with ligands. A wide discussion of the role of these processes is given in B. W. Bache's work (1986).

This paper is mostly focussed on the conditions of solubility and mobilization of aluminium with respect to equilibrium analysis of mineral phases in the weathering zone of the pyrite-bearing schists. Most of aluminium minerals appearing in crystalline rocks have very low solubility. Some amount of aluminium is released during their decomposition which results in a limited number of more soluble minerals being formed; they are more stable in contact with water under supergene conditions. The rate of decomposition of primary minerals as well as of transformation of mineral composition of rocks is strongly dependent on pH and Eh of the environment and on water circulation and recharge conditions.

A number of extensive studies have been conducted so far on solubility of minerals that contain aluminium, in particular with respect to the conditions of mobilization of aluminium in a soil environment which is under the influence of acid atmospheric precipitation. Much attention was directed to the solubility of aluminium hydroxide (as in the work by H. M. May *et al.*, 1979). However, results of experimental studies often did not confirm theoretical assumptions, in particular, for cases when pH was between 5 and 7. One of the most probable reasons for high concentration of aluminium in waters at near-neutral pH is that other mineral phases control the solubility of aluminium. Most waters contain dissolved silica, and it can be in equilibrium with such aluminosilicates as kaolinite or montmorillonite. An analysis of stability of those minerals in term of pH and of Al and Si concentrations indicates that the solubility of aluminium goes down with increased silica concentration (W. L. Lindsay, 1979). Despite the pertinence of this conclusion, it should be noted that Al

Table 1

Chemical composition of waters from the Purpurowe Lake and effluents

Components [mg/l]	Purpurowe Lake		Effluents in spoil banks				Effluents in the quarry	
			no. 1		no. 2			
	min.	max.	min.	max.	min.	max.	min.	max.
	conductivity [µS/cm]							
	2960	5000	3620	3720	4160	4590	2560	3190
	pH							
	2.55	2.84	2.62	2.98	2.72	2.89	2.50	2.58
SiO_2	53	87	59	83	45	64	44	56.6
Ca	96	309	173	346	160	403	88	184
Mg	108	256	173	183	248	345	68	109
Na	4.69	8.20	5.6	6.5	4.4	5.6	4.0	5.2
K	0.10	0.90	0.46	0.6	2.3	2.61	0.08	0.3
SO_4	1733	4535	2389	2671	3411	4520	1247	1998
Cl	3.1	14.8	x	7.6	2.3	4.8	4.5	10.2
PO_4	0.26	2.72	0.10	0.20	0.10	0.35	0.11	1.52
F	0.49	2.64	1.18	1.96	1.05	1.50	0.85	1.15
Al	51.5	176	65.7	94	49	77	31.9	58
Fe	183	601	231	236	579	1023	122	309
Mn	1.96	4.97	3.48	4.95	8.18	14.2	0.72	1.01
Li	0.032	0.065	x	0.040	x	0.040	0.019	0.029
Sr	0.20	0.32	0.35	0.41	0.51	0.77	0.12	0.14
Cu	1.68	6.32	1.84	2.45	1.44	2.57	0.49	1.88
Zn	0.37	1.65	0.49	0.60	1.03	1.12	0.13	0.26
Ni	0.20	0.58	0.23	0.40	0.32	0.50	0.10	0.18

x — traces

concentration at pH around 6–7 is commonly greater than that which could be concluded from the solubility of aluminosilicates.

Discussing the question of lack of equilibrium between waters and solid phases, T. Pačes (1978) suggested consideration of the presence of a phase of reversible cryptocrystalline aluminosilicate $[Al(OH)_3]_{1-x}$ $[SiO_2]_x$, whose composition is variable and pH-dependent. The Al concentrations in terms of pH at different concentrations of silica, as calculated from the solubility of this phase, fit the experimental data pretty well. In addition, the same comparison shows decrease of Al solubility with increase of silica concentration. A subsequent study by V. C. Farmer *et al.* (1983) of imogolite, $(OH)_3Al_2SiOH$, reveals the ability of aluminium to migrate through acid soils in the form of soluble silica complexes. The existance of such silica complexes may be one of the possible reasons for high concentration of dissolved aluminium at pH around 6.

The presence of sulphates in acid waters essentially alters the solubility of both hydroxides and aluminosilicates. In waters discharged from areas affected by significant dry deposition of SO_2 or by significant deposition of sulphates supplied with rains, the concentration of sulphate ion often exceeds 10^{-4} M. Concentration of sulphates is even greater in waters flowing from zones of oxidation of sulphides; a common concentration reaches the value of 10^{-2} M. Under such circumstances the stable phases of sulphate minerals can be formed (N. van Breemen, 1973; E. Eriksson, 1981; D. K. Nordstrom, 1982). The effect of those minerals on Al concentration starting from sulphate concentration of the order of 10^{-4} M and pH less than 4 consists in keeping aluminium concentration in lower equilibrium than would be possible at the equilibrium with hydroxides and aluminosilicates.

DISCUSSION OF RESULTS

Waters in the area of the pyrite-bearing schist mine can be divided into two distinct groups: (1) waters in the Purpurowe Lake and effluents from the quarries and spoil banks and (2) waters in the upper course of the Rdzawy Stream.

Characteristic features of the first group include: pH from 2.50 to 2.98 (average 2.63); high total dissolved solids value (TDS), from 1518 to 5815 mg/l; very high concentration of aluminium, from $1.18 \cdot 10^{-3}$ to $6.52 \cdot 10^{-3}$ M (31.9–176.0 mg/l); high concentration of sulphates (1247–4535 mg/l; average 2726 mg/l); there is also a high concentration of Fe and distinct enrichment in other metals (Mn, Cu, Zn, Ni; Tab. 1). Due to clear difference between chemical composition of waters in the two effluents from the spoil banks area, their relevant data (items 1 and 2 on Fig. 1) were shown in Table 1 separated from each other.

Water in the Rdzawy Stream is of decidedly lower mineralization, with TDS in the range of 124–222 mg/l; pH is between 3.96 and 5.28 (E. Balcerzak *et al.*, 1992). The given values for TDS are based on computation with the use of the WATEQ4F computer program.

In chemical composition of all waters, sulphates are dominant among anions; calcium and magnesium are dominant among cations. Water samples from the Rdzawy Stream represent groundwater discharged from the water-bearing rubble horizon. Its composition reflects some transformation connected with chemical weathering taking place at the outcrop of the pyrite-bearing schists. Low mineralization results from intesive water exchange in the rubble water-bearing horizon which is recharged by infiltration. Chemistry of waters from the Purpurowe Lake and all effluents indicates a stronger transformation.

A deep cut in the formation by the quarry to a depth of 30–60 m has caused changes in hydrogeological conditions within the area of the cone of depression, intensified physical and chemical weathering of exposed rocks, and consequently enhanced changes in chemical composition of water in that part of the deposit which was subject to exploitation. Chemistry of water is clearly determined by the decomposition of pyrite, which under such circumstances is intensified. Oxidation of pyrite and other ore minerals leads to acidification of the environment by sulphuric acid; thus, it acts in favour of decomposition of most of the primary minerals.

Rate of saturation of water witb respect to minerals is an indicator of their chemical stability in a given environment. It is expressed by a saturation index (SI) which is SI = log (IAP/K), where: IAP — ion-activity product, K — equilibrium constant. SI values for selected minerals are shown on Figure 2. It was assumed that equilibrium with respect to a particular mineral is reached when its SI value is in the range of ±5% log K. E. A. Jenne *et* *al.* (1980) concluded that fluctuations of saturation index around zero, for waters in equilibrium with minerals increase together with the increase of solubility of the mineral phase. The same authors determined that the value of 5% log K corresponds with the permissible limit of fluctuation at the equilibrium with a given phase. The limits of ranges of fluctuation are shown on the diagram with dashed lines running on both sides of the equilibrium line that represents SI = 0.

Figure 2 shows, among other things, SI values for waters in the Purpurowe Lake and the effluents. Data for chlorite have not been included in the figure since saturation index values were recorded below –55. Waters are significantly undersaturated with respect to all aluminosilicates under consideration. This may illustrate a strong tendency for decomposition of main minerals making up the schists including chlorites, sericite, and feldspars. From calculation, a conclusion can be drawn that waters in the Purpurowe Lake and the effluents are also undersaturated with respect to such secondary minerals as: illite, calcium montmorillonite, or even kaolinite.

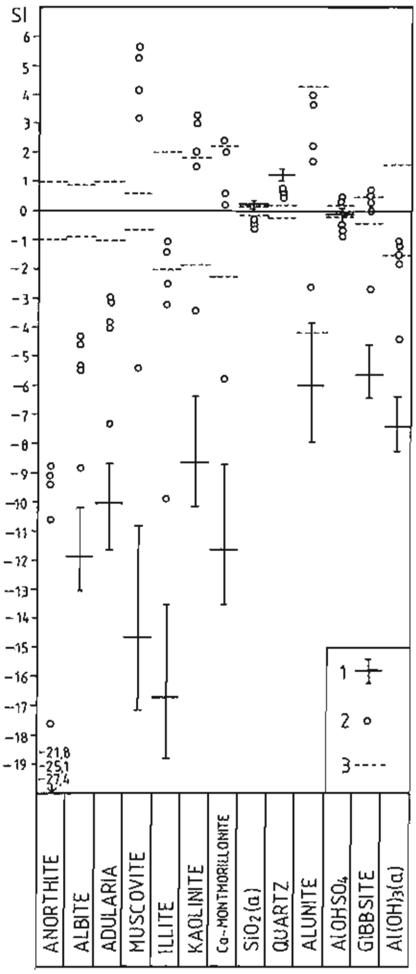

Fig. 2. Disequilibrium indices of selected minerals

1 — average disequilibrium indices for waters from the Purpurowe Lake and all effluents, with variation range indicated, 2 — disequilibrium indices for waters from the Rdzawy Stream, 3 — limits of the SI value ranges corresponding to permissive equilibrium with individual minerals

Wskaźniki nasycenia wybranyeh minerałów

1 — średnie wskaźniki nasycenia dla wód z Jeziorka Purpurowego i wszystkich wyeieków, z podaniem przedziału zmienności, 2 — wskaźniki nasycenia dla wód z Potoku Rdzawego, 3 — granice przedziałów wartości SI odpowiadających równowadze z poszczególnymi minerałami

Kaolinite has been found among other secondary minerals of the pyrite deposit at Wieściszowice. There are kaolinized patches in the schists, reaching a thickness of 1–2 m (R. Nielubowicz, 1954). Kaolinite has also been found in the bottom sediments of the Rdzawy Stream and at the spoil banks where it forms concentrations of several centimetres in diameter. The undersaturation of waters under study with respect to kaolinite is not at odds with its occurrence. Kaolinite becomes unstable in acid water with a high concentration of sulphate. Under such circumstances its position in controlling the solubility of aluminium is taken over by sulphate minerals that do not allow for the increase of Al concentration to the rate at which waters could reach saturation with respect to kaolinite (a broad discussion of the role of the sulphate minerals is offered in a later section of this paper). Water samples from the Purpurowe Lake and the effluents, with high concentration of sulphates and very low pH, do not represent favourable conditions for kaolinite to be formed. This mineral was found at places where similar high concentration of SO_4^{2-} ion did not occur in waters. Concentration of sulphates in the Rdzawy Stream waters are 20 to 90 times less than that in the Purpurowe Lake and the effluent waters.

In spite of simultaneously lower concentrations of aluminium and evidently higher pH, the stream waters are commonly supersaturated with respect to kaolinite (Fig. 2). Kaolinized patches of the deposit prove that hydrogeochemical conditions dominating in the weathering zone prior to commencement of exploitation were quite different than that at present. Products of decomposition of pyrite were gradually removed from zones favourable for water circulation; in such a way conditions were created that provided stability for kaolinite.

At present, formation of kaolinite in a similar way at the surface of spoil banks is likely to occur; most probably, this is due to oxidation of disintegrated rock material and flushing by infiltrating water from precipitation.

During decomposition of aluminosilicates, large quantities of silica are released to waters existing in the mine area (Tab. 1). These waters are saturated with respect to amorphous silica and supersaturated with respect to quartz (Fig. 2). The twentyfold higher solubility of amorphous silica than that of quartz is the reason why most natural waters appear to be undersaturated with respect to this amorphous form of silica. It is expected that amorphous silica undoubtedly controls high concentrations of SiO_2 in waters under study. Calculation of ion equilibrium indicates that waters are strongly undersaturated with respect to alunite, gibbsite, and $Al(OH)_{3(a)}$. The absence of alunite in the weathering zone as well as the undersaturation with respect to this mineral undoubtedly results from low concentration of potassium in both the rocks and the waters. Sericite, being a basic carrier of potassium in the ore-bearing rocks, is the least susceptible to weathering among aluminosilicates occurring in the area. Crystalline as well as amorphous forms of $Al(OH)_3$ can be stable at significantly higher pH. Such may be the case of gibbsite; if activity of sulphates is around 10^{-2} M, i.e. very close to that occurring in waters under present study, then gibbsite is stable at $pH > 5.7$ (D. K. Nordstrom, 1982).

A number of studies related to solubility of aluminium in acid sulphate waters (M. W. Gang, D. Langmuir, H. L Crouse, A. Rose *fide* D. K. Nordstrom, 1982; E. Eriksson, 1981) have revealed that at pH < 4–4.5 a sulphate mineral phase can be formed that is responsible for the control of this element's concentration; this phase is of lesser solubility than that of gibbsite or kaolinite. This finding is in agreement with the results of the present study. Concentrations of Al^{3+} ion in waters from both the Purpurowe Lake and the effluents have been found much lower than could be concluded from gibbsite and kaolinite solubility. Activities of aluminium versus pH group close to the line which reflects the solubility of basic aluminium sulphate, $AlOHSO_4$, at the average sulphate ion activity in these waters, which is equivalent to $7.78 \cdot 10^{-3}$ M ($p[SO_4^{2-}] = 2.109$ (Fig. 3).

It was N. van Breemen (1973) who noted that chemical composition of waters originating from acid sulphate soils as well as from acid mining residues is very close to the reaction $p[Al^{3+}] + p[OH^-] + p[SO_4^{2-}] = 17.23 \pm 0.16$. This could be indicative of equilibrium between dissolved aluminium and basic aluminium sulphate $AlOHSO_4$, ac-

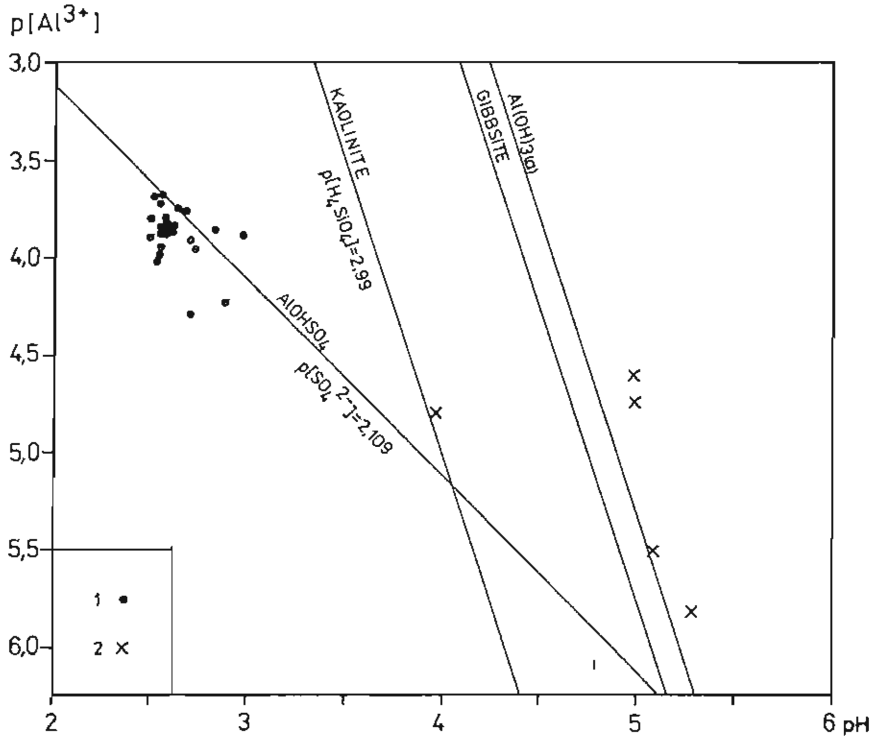

Fig. 3. Activity of the aluminium ion as a function of the pH in solutions in equilibrium with different aluminium minerals
1 — waters from the Purpurowe Lake and effluents, 2 — waters from the Rdzawy Stream
Aktywność jonu glinowego jako funkcja pH roztworów w równowadze z różnymi minerałami glinu
1 — wody Jeziorka Purpurowego i wycieków, 2 — wody Potoku Rdzawego

cording to the reaction $AlOHSO_4 = Al^{3+} + OH^- + SO_4^{2-}$. Value of pK (after N. van Breemen) is equal to 17.23, with standard deviation of 0.16. According to other authors, pK for $AlOHSO_4$ is from 17.23 to 17.80. Agreement with the quoted figures was reached in the case of waters from both Purpurowe Lake and the effluents. The average sum for p[Al^{3+}] + p[OH^-] + p[SO_4^{2-}] is 17.37±0.19; at the same time $pAlOHSO_4$ for particular water samples was between 17.08 and 17.82. The mineral phase as suggested by N. van Breemen (1973) that controls dissolved aluminium in waters of acid sulphate soils and in acid mine waters corresponds in both composition and solubility to jurbanite, $AlOHSO_4 \cdot 5H_2O$. This mineral was identified not long ago (J. W. Anthony, W. J. McLean, 1976). Jurbanite appears to be stable in a wide range of low pH values: below 3.3 at a sulphate activity equal to 10^{-4} M, and below 4.0 at a sulphate activity equal to 10^{-2} M (D. K. Nordstrom, 1982).

Figure 4 shows solubility curves for selected aluminium minerals including $AlOHSO_4$, based on the equation $pAl + pOH + pSO_4 = 17.23$. Variability of ($pAl + 3pOH$) versus ($2pH + pSO_4$) is also shown for both groups of waters.

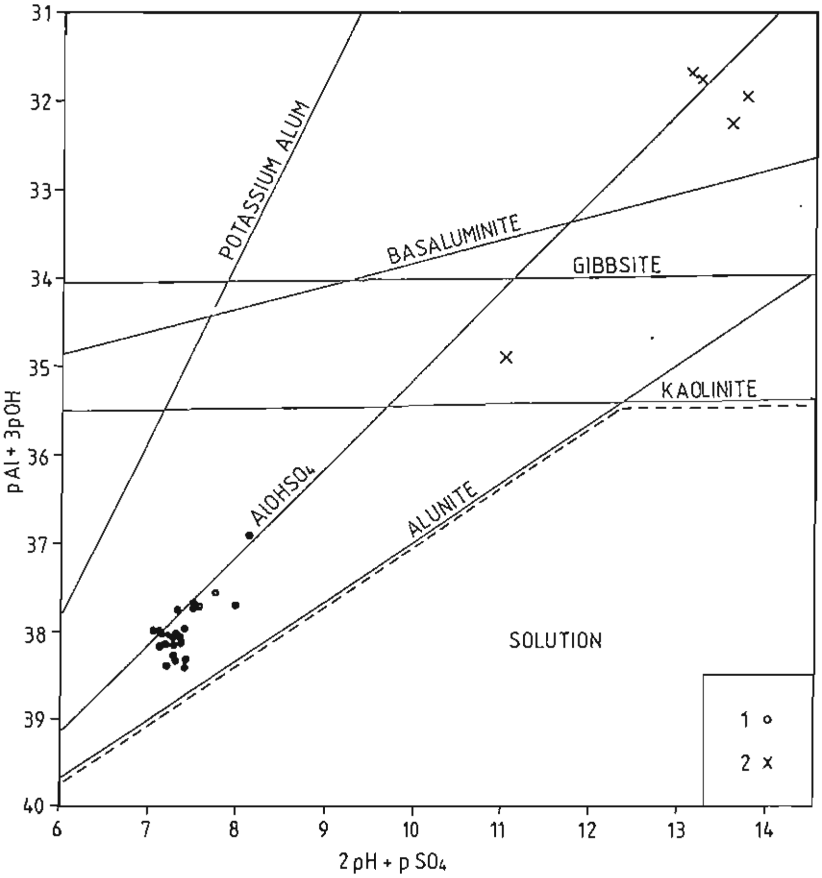

Fig. 4. Solubility diagram for basaluminite, potassium alum, gibbsite, alunite, kaolinite and AlOHSO4 (after N. van Breemen, 1973)

Explanations as in Fig. 3

Diagram rozpuszczalności basaluminitu, ałunu potasowego, gibbsytu, alunitu, kaolinitu i AlOHSO4 (według N. van Breemena, 1973)

Objaśnienia jak na fig. 3

At p[SO_4^{2-}] = 2.109 and pH = 2.63, waters from the Purpurowe Lake and the effluents fall inside the field of jurbanite's stability on Nordstrom's diagram of mineral stability (D. K. Nordstrom, 1982) arranged for the system $Al_2O_3 - SO_3 - H_2O$ at 25°C.

Waters from the mine show a state of saturation with respect to $AlOHSO_4$ or are very close to saturation. Saturation index (SI) ranges from −0.589 to 0.148. Activity of aluminium ion in waters and rate of saturation with respect to $AlOHSO_4$ are governed by concentration of sulphate (Fig. 5). Based on assumptions given before, SI in the range of ±0.162 is considered as corresponding to the waters' equilibrium with respect to $AlOHSO_4$. For most of the waters, SI_{AlOHSO_4} is contained within the said limits; this deals with waters from the

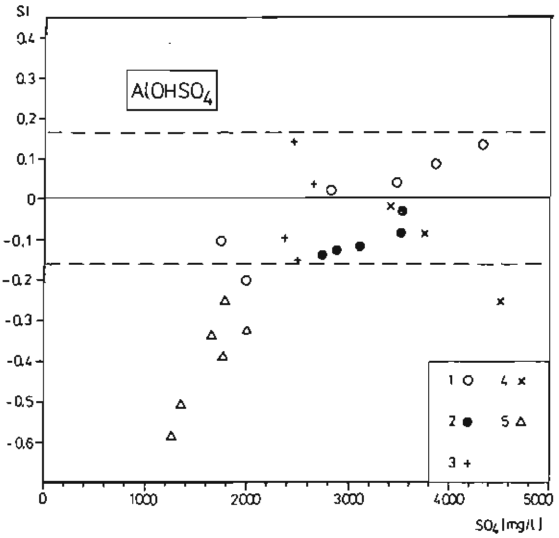

Fig. 5. Disequilibrium indices of AlOHSO4 as a function of the sulphate concentration in waters
1 — waters from the Purpurowe Lake, autumn-winter period, 2 — waters from the Purpurowe Lake, summer period, 3 — effluent no. 1 in the spoil bank, 4 — effluent no. 2 in the spoil bank, 5 — effluents in the quarry
Wskaźniki nasycenia AlOHSO4 w funkcji stężenia siarczanów w wodach
1 — wody Jeziorka Purpurowego, okres jesienno-zimowy, 2 — wody Jeziorka Purpurowego, okres letni, 3 — wyciek nr 1 na hałdzie, 4 — wyciek nr 2 na hałdzie, 5 — wycieki w kamieniołomie

Purpurowe Lake and the effluents from the spoil banks. Values of SI > 0 appear only occasionally, during autumn and winter seasons (as in the case of samples from the Purpurowe Lake and effluent no. 1 from the spoil bank). It can generally be concluded that waters are saturated with respect to $AlOHSO_4$. They could reach the state of equilibrium due to sufficiently long contact with mineral material. Undersaturated with respect to $AlOHSO_4$ are waters in the effluents, discharged from the fissured water-bearing horizon due to the deep cut in the formation by the quarry. In general, they are of the same character as remaining waters in the same group. Clearly visible lower concentration of sulphates and subsequent undersaturation of waters can be concluded from the fact that these waters have remained in shorter contact with weathering rock material of the ore-bearing body.

In spite of the position which, in the light of the above consideration, is most likely played by the jurbanite in controlling the solubility of aluminium, so far there is a lack of information on this mineral's occurrence at Wieściszowice. The following aluminium sulphate minerals were found in the weathering zone of ore-bearing body: alunogen $Al_2(SO_4)_3 \cdot 18H_2O$ and pickeringite $MgAl(SO_4)_2 \cdot 22H_2O$. They appear in the form of fine-crystalline encrustations and efflorescences on the walls of the quarry and the spoil banks. Their crystallization is taking place due to evaporation of pore solutions. Most of supergene sulphate minerals are unstable under variable atmospheric conditions; this results in substantial permanent chemical and mineralogic transformations taking place within this paragenesis. Formation of other aluminium sulphates such as pickeringite and alunogen, more stable then jurbanite, is most likely the reason why occurrence of jurbanite has not been recorded. Chemistry of atmospheric waters infiltrating the ore-bearing rocks in the mine area is subjected to dynamic transformations during movement of these waters to discharge zones. Lack of conditions favourable for permanent supersaturation of waters with respect to jurbanite may also be a reason for the absence of this mineral.

Contrary to waters from the mine area, waters in the Rdzawy Stream contain much less aluminium (from $1.48 \cdot 10^{-5}$ to $1.22 \cdot 10^{-4}$ M; 0.4–3.3 mg/l) and sulphate (from 51 to 129 mg/l) (E. Balcerzak *et al.*, 1992). Their pH is higher (3.96–5.28). There are insignificant differences among water samples collected from the upper course of the Rdzawy Stream (E. Balcerzak *et al.*, 1992) and these differences deal with concentrations of sulphate, aluminium, iron and silica; however, waters are, in general, of the same character. Variations in composition and pH are the reason for some differentiation in rate of saturation of these waters with respect to different minerals (Fig. 2). For most of aluminium minerals under consideration, these waters have higher SI values than that in waters from the Purpurowe Lake and the effluents. Waters from the Rdzawy Stream show undersaturation with respect to feldspars, illite, and chlorite; chlorite has not been included in Figure 2 due to its very low SI (< –30). Most water samples from the stream appear to be supersaturated with respect to muscovite and kaolinite, and saturated with respect to Ca-montmorillonite. These waters, with lesser concentration of SiO_2 than that in waters from the Purpurowe Lake and the effluents from the spoil banks and the quarry, are only insignificantly supersaturated with respect to quartz and undersaturated with respect to amorphous silica. The SI value might indicate that they are in near-equilibrium state with respect to gibbsite and $Al(OH)_{3(a)}$; this could confirm the fact that behaviour of gibbsite at sulphate activities around 10^{-4} M is stable at pH higher than 4.5 (D. K. Nordstrom, 1982). The analysis of ion equilibrium could also indicate the theoretical stability of alunite.

In its upper course, the Rdzawy Stream discharges water from the water-bearing rubble horizon existing in the zone of the outcrop of the ore body. Based on the analysis of saturation state of its water, a conclusion can be drawn that most likely the chemical composition of water is a reflection of conditions that dominated in the weathering zone in the mine area before exploitation was started. The exploitation of pyrite-bearing schists became a factor which intensified the process of weathering. As a result, a number of alterations can be observed in the mineral paragenesis and in chemistry of waters. A high concentration of aluminium in waters exhibits one such alteration.

RECAPITULATION

The ore body of pyrite-bearing schists at Wieściszowice is an interesting object on the statewide scale, due to the scale of oxidation processes of sulphides and development of the weathering zone.

Acidification of the environment due to oxidation of pyrite increases the rate of decomposition processes of most primary minerals occurring in the ore body. Particularly intensive processes are taking place in the abandoned quarry and accompanying spoil banks. Strongly acidic sulphate waters in the area of the old mine contain an assemblage of metals in increased concentrations, including very high concentration of aluminium. The analysis of ion equilibrium reveals that under existing conditions the basic aluminium sulphate $AlOHSO_4$ is responsible for the control of concentration of aluminium.

Chemistry of waters in the Rdzawy Stream which discharge waters outside the mine area from the rubble water-bearing horizon at the outcrop of the pyrite-bearing schists offers evidence that under conditions undisturbed by exploitation (i.e., under natural weathering processes) the concentration of aluminium remains controlled by the clay minerals, most likely the kaolinite.

Weathering processes of exposed rocks and of material deposited as spoil banks, intensified as a result of exploitation, lead to mobilization of many elements that are mobile in an acid environment. Thcy are responsible for pollution of waters discharged from the mine area; polluted waters create a serious hazard to quality of water in the Mienica river flowing through Wieściszowice.

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ROZPUSZCZALNOŚĆ GLINU W KWAŚNYCH WODACH Z KOPALNI PIRYTU W WIEŚCISZOWICACH (RUDAWY JANOWICKIE, SUDETY ZACHODNIE)

Streszczenie

Obszarem badań była opuszczona kopalnia pirytu w Wieściszowicach (Rudawy Janowickie). Pozostałością po niej są trzy kamieniołomy oraz rozległe hałdy przerobionych łupków. Złoże serycytowo-chlorytowych łupków pirytonośnych położone jest wśród skał metamorficznej osłony granitoidowego masywu Karkonoszy.

Analizom poddano próbki wód z Jeziorka Purpurowego zajmującego największy, północny kamieniołom oraz z wycieków na hałdach i w kamieniołomie. Aktywności jonów i wskaźniki nasycenia faz mineralnych zostały obliczone przy użyciu programu WATEQ4F. Napotkano wody silnie kwaśne (pH 2,50–2,98) o podwyższonej mineralizacji (1500–5800 mg/l TDS). W ich składzie chemicznym dominują siarczany, wapń i magnez. Wody te charakteryzują się również wysokimi stężeniami glinu i żelaza oraz wyraźnym wzbogaceniem w mangan, miedź, cynk i nikiel.

W kwaśnym środowisku większość pierwotnych minerałów łupków podlega rozkładowi hydrolitycznemu. Intensywne procesy wietrzenia skał odsłoniętych w kamieniołomie i materiału zdeponowanego na hałdach prowadzą do uruchamiania szeregu pierwiastków, w tym glinu. Analiza równowagi jonowej wskazuje, że rozpuszczalność glinu w kwaśnych wodach z Jeziorka Purpurowego oraz z wycieków w kamieniołomie i na hałdach jest kontrolowana przez zasadowy siarczan glinowy $AlOHSO_4$. Stężenia glinu w Potoku Rdzawym, drenującym wody z poziomu rumoszowego na wychodniach łupków poza obszarem kopalni, regulowane są przez minerały ilaste, prawdopodobnie kaolinit.

Zanieczyszczone metalami wody z rejonu kopalni stanowią zagrożenie dla jakości wód Mienicy, przepływającej przez Wieściszowice.