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**GEOCHEMICALLY UNSTABLE MINERALS IN CARBONIFEROUS
ROCKS IN THE LIGHT OF PROGNOSED ENVIRONMENTAL
IMPACT OF COAL MINING WASTES**

INTRODUCTION

Polymorphs of iron sulfides (pyrite and marcasite), despite of occurring in waste carboniferous rocks in the amounts generally not higher than 1 % S_t, due to their geochemical instability in contact with atmospheric air and water at the mining waste dumps, exert long-term adverse impact on the aquatic environment, lasting for decades. Sulfide oxidation results in generation and leaching of sulfates and hydronium ions that leads to high sulfate salinity of leachate, and in case of insufficient buffering capacity and gradual depletion of available buffering minerals - calcite and dolomite, cause time-delayed development of Acid Rock Drainage (ARD) and subsequent heavy metal (HM) mobilization from the waste rock and bedrock. This often results in dramatic increase of pollution potential and aquifer deterioration in old and abandoned dumping sites. Environmental impact assessment of the dumping site in order to apply adequate protection measures requires correct short- and long-term prognosis of contaminant leaching behavior that is controlled primarily by sulfide oxidation. Here, factors affecting sulfide oxidation have been discussed and a computer simulation of ARD generation tested on low-buffered coal mining waste disposed at the Smolnica dump, USCB, Poland, at the background of sulfide reactivity.

MATERIAL AND METHODS

The kinetics of sulfide oxidation (reactivity) is described by the first-order reaction $(G_S)_t = (G_S)_0 \exp(-kt)$ and can be characterized by sulfide half-life $t_{0.5}$ that can range widely, for carboniferous seams of USCB roughly from 30 to 10500 days, mean value 590 days. The actual kinetics was found to be largely depend on the specific surface, textural and structural mode of sulfide crystals that is often connected with a coal seam position in the stratigraphic sequence of carboniferous strata. Among syndiagenetic, anadiagenetic and catadiagenetic forms of sulfides, the first one is the most reactive; the highest susceptibility to oxidation show low-crystalline metacolloidal, framboidal and dispersed textural types of sulfides occurring mostly in argillaceous rocks and coal; coarse-grained crystals are the

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least reactive, though no direct correlation between sulfide reactivity and its type can be derived. At the coal mining waste dump, the availability of air and water also affects the kinetics of sulfide oxidation (Twardowska et al., 1988). The tested coal mining wastes disposed at the 38 years old Smolnica dump originate from the Westphalian stratigraphic section, Upper Silesia mudstone series and represent argillaceous and arenaceous hard rocks in the form of mudstone, sandstone and siltstone. The sulfide reactivity within the medium range and low buffering capacity determines their high ARD generation potential (Table 1.)

Table 1 Basic parameters controlling ARD generation in the tested wastes

Sulfide sulfur content	Sulfide reactivity	Buffering capacity	Buffering ratio	Porosity
$(G_s)_0$ [% wt.]	$t_{0,5}$ [days]	G_{buf} [eq/t]	$\zeta_{buf} = G_{buf}/G_s$	N [%]
0,866	1440	421,7	0.70	0.3

Simulation of sulfide decomposition was performed with use of PHREEQC Interactive v. 2.7.1.1(2003) geochemical computer program that unlikely other popular programs based on mineral equilibria, e.g. WATEQ 4F, MINTEQA2 etc., considers also reaction kinetics (Parkhurst and Appelo, 1999), and tested on the data obtained from over 12 years' lysimetric studies on fresh and 10-years' old wastes (Szczepańska et al., 1996).

RESULTS

Results of 50 years' modeling of pH changes, ferrous/ferric iron and sulfide/sulfate sulfur generation pattern in pore solution (Fig. 1, 2, 3), and secondary minerals, mainly goethite and melanterite formation due to pyrite oxidation, simulate the actual kinetics of the process occurring in coal mining waste disposed at the Smolnica dump and derived from the lysimetric studies.

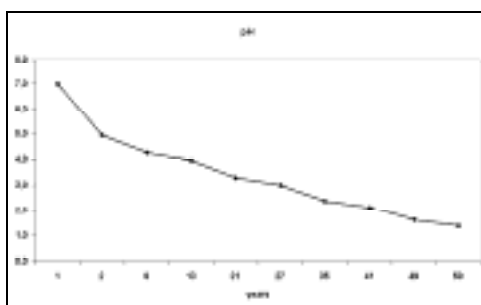


Fig. 1 Simulation of long-term pH changes due to pyrite oxidation in coal mining waste at the Smolnica dump (PHREEQC Computer Program, 2003)

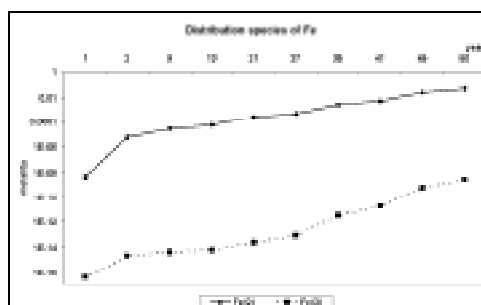


Fig. 2 Simulation of long-term Fe²⁺/Fe³⁺ changes due to pyrite oxidation in coal mining waste at the Smolnica dump (PHREEQC Computer Program, 2003)

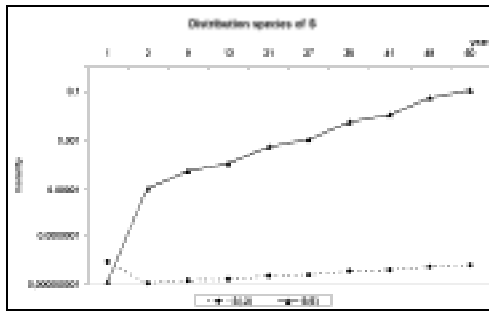


Fig. 3 Simulation of long-term S^2/S^{-6} changes due to pyrite oxidation in coal mining waste at the Smolnica dump (PHREEQC Computer Program, 2003)

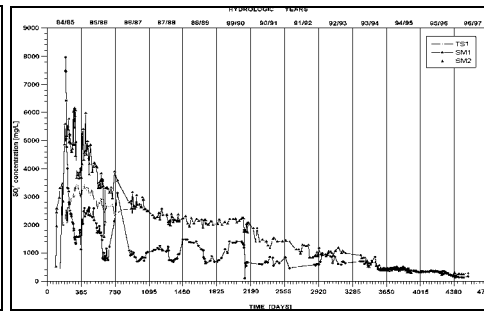


Fig. 4. Sulfate leaching from the surface coal mining waste layer 1.5 m thick of different buffering capacity. Long-term lysimetric studies within the 12 years' natural hydrologic cycle (1984-1996) (after Szczepańska et al, 1996)

The presented computer simulation was focused on the processes where entirely pyrite oxidation was involved. Neither buffering by carbonate minerals, nor leaching behavior of sulfates were addressed at this stage. This step is subject to further geochemical modeling with use of the data on long-term leaching behavior of this waste within 12 and 22 years of disposal observed in the long-term lysimetric studies (Fig. 4, after Szczepańska et. al, 1996).

CONCLUSION

PHREEQC Geochemical computer program has been proved to be a reliable tool for simulation of ARD generation resulted from sulfide oxidation in waste carboniferous rocks and thus can be used as a tool for long-term prediction of their pollution potential. The predictive simulation requires also a correct estimation of buffering minerals availability for reaction with the generated acid, which in a complex and heterogeneous rock cannot be assessed on the basis of pure stoichiometric calculations.

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