Natural Neutralization of Acid Mine Water in Carbonate Deposits of Kizel Coal Basin

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Abstract

Processes affecting neutralization of acidic mine drainage (AMD) were evaluated within the overburden fissure-karst limestones. Flow of AMD from flooded mines into overlying carbonate deposits occurs in zone of large faults in the Kospashskoye coalfield of Kizel coal basin. In order to understand the geochemical processes occurring within the limestone aquifer the mine water flows into, the chemical data of effluents emerged from ascending springs were processed by geochemical modeling. To evaluate the degree of possible AMD dilution by neutral-to slightly alkaline ambient groundwater and its affect to acid neutralization, their mixing in different ratio was simulated. Simulation of AMD reaction with calcite has showed possible pH and compositions of neutralised mine water. The results of the modeling were compared with measured chemical data of spring effluents. Calculations of saturation index of the effluents with respect to most common secondary minerals identified the potential form of metals precipitation.

Keywords: AMD, carbonate deposits, neutralization, dilution ratio, saturation index, PHREEQC modeling

Introduction

The formation of acid mine drainage (AMD) is a common problem for coal and sulphide ore mining regions (Cravotta and Trahan 1999, Cravotta and Ward 2008). The AMD typically contains elevated concentrations of dissolved and particulate Fe and dissolved SO_4^{2-} produced by the oxidation pyrite (Cravotta and Trahan 1999). The processes of pyrite oxidation and formation of AMD have been extensively studied and described (Singer and Stumm 1970, Evangelou and Zhang 1995, Blowes and Ptacek 2003). However, the quality of the mine drainage depends in large part on the reactions with minerals capable of neutralizing the acidic water (Sherlock et al. 1995). Carbonate rock dissolutions can increase pH and concentrations of alkalinity (HCO_3^-, CO_3^{2-}, OH^-) of mine water (Cravotta and Ward 2008). The neutralized AMD has circum-neutral or alkaline pH values and is usually called neutral mine drainage (NMD) (Banks et al. 2002). Other geochemical reactions that contribute to formation of NMD are: a low content of sulphide minerals, neutralization of acid by naturally highly alkaline groundwater, dissolution basic silicate minerals (Banks et al. 2002), CO_2 degassing, precipitation of gypsum, dissolution of metal hydroxides ($Fe(OH)_3$, $Al(OH)_3$) and oxyhydroxides (FeOOH, AlOOH) (Stumm and Morgan 1996; Blowes and Ptachek 2003). Inversely, precipitation of the (oxy)hydroxides and hydroxysulfates is accompanied by the release of protons H^+ (Stumm and Morgan 1996; Blowes and Ptachek 2003; Bigham et al. 1996). Co-precipitation metals can occur together with the precipitation of hydroxide and hydroxysulfate minerals. Precipitation of the secondary compounds can coat or armor the limestone surfaces, decreasing the rate and extent of limestone dissolution and alkalinity production (Cravotta and Ward 2008).

Understanding the processes that cause changes in chemical composition of mine water is essential for making decisions about remediation activities. This paper considers neutralization of the acid mine water flowing into overburden fissure-karst carbonate aquifer. Scientific researches related to the study of hydrogeochemical processes occurring in the carbonate deposits overlying the coal strata and controlling acid neutralization of the mine drainage are almost absent for the study area. In order to evaluate geochemical processes occurring within the carbonate aquifer and its effect on AMD quality, chemical composition of the effluents from two springs was thoroughly studied and processed using methods of hydrochemical modeling.

Description of Study Area

The Kospashskoye coalfield is located in the northeast part of Kizel coal basin in Perm Kray, Russia. The main structure of the Kospashskoye coalfield is a synclinal fold, the western flank of which is dislocated by a thrust with an amplitude of up to 600 m (Imaikin and Imaikin 2013). The coal-bearing strata occur within the formations of the Lower and Middle substage of the Visean (C_1v_{1-2}). The rocks of the coal strata include pyrite and organic sulphur. An aquifer system of the coal-bearing strata (C_1v_{1-2}) comprises sandstone beds separated from each other by layers of argillite and coal. In the area under study, the coal strata are overlaid by carbonate deposits of the Upper Visean substage (C_1v_3) and the Serpukhovian stage (C_1s) that constitute a carbonate fissure–karstic aquifer (Cv_1+s). On a flank of the syncline, the Visean coal-bearing strata occupy a higher position relative to the Visean-Serpukhovian deposits in the centre of the structure. In natural undisturbed conditions, the karstic aquifer in the Visean-Serpukhovian rocks is separated from the aquifer of the coal-bearing strata by a layer of low permeable bituminous rocks. In zones of large faults, this aquitard is interrupted and the considered aquifers are hydraulically connected. Due to the hydraulic connection, mine water (AMD) can migrate into the karstic limstone aquifer influencing the groundwater quality in it.

The mines in the Kospashskoye coalfield were operated from 1939 to 1998. The cessation of groundwater pumping after the mines closure has resulted in gradual recovery of piesometric level and formation of a number of ascending springs with both clean and acidic groundwater. The research focused on two of the springs, which in a previous study (Imaikin and Imaikin 2013) are identified as discharges of groundwater extremely contaminated by AMD. They are located in the valleys of East Kizel and Poludny Kizel rivers where the Visean-Serpukhovian limestone outcrops.

Materials and methods

In this investigation, the geochemical data of clean groundwater (Cv_1+s, well 5g), springs water (spr. 29 and spr. 31), and mine water from the “Kospashskaya” mine (one of the mines in the Kospashskoye coalfield) for the period of 2011-2013 years were studied and processed. Hydrochemical monitoring in the area of the coalfield have been performed by Inter-industry Scientific Research Institute of Environment of the Fuel and Energy Complex (original abbr. “MNIIEKO TEK”). Chemical analyzes of the water samples were carried out in the analytical laboratory of the Ural Center for Socio-Ecological Monitoring of Coal Mining Areas (2011) and Analytical Laboratory of LLC “Permenergoaudit” (2012-2013). Inductively coupled plasma-atomic emission spectroscopy was applied for the water quality control. The mean chemical composition of the considered water samples is presented in Table 1.

In order to determine the saturation state of the uncontaminated groundwater (Cv_1+s), springs effluents, and the mine water (AMD) with respect to selected minerals, the saturation index (SI) calculations were made. The results of geochemical calculations are shown in Table 1. To assess the degree of possible dilution of the AMD by uncontaminated groundwater or, conversely, the degree of pollution of the groundwater by the mine water, modeling of their mixing in various proportions was performed. At the next stage, modeling of interaction of the mine water with calcite was carried out. The data obtained as a result of the simulations were compared with the actual data of chemical composition of the springs. All simulations were performed using the PHREEQC geochemical code (Parkhurst and Appelo 2013) with the WATEQ4F thermodynamic database (Ball and Nordstrom 1991). Eh (redox) was not measured in the field. In the processing, the values of redox potential were found for each analysis using the activities of ammonium (NH_4^+) − nitrate (NO_3^-) redox couple.

Results and discussion

Having evaluated the groundwater quality data (table 1), we found two springs effluents with pH ranging from acidic to circum-neutral. A circum-neutral effluent is not common to be observed among the acidic mine drainages from the pyrite-rich mines of coalfield. The following characteristics of the effluent should be noted: the pH of the effluent in the spring 29 is mostly acidic (4.0 – 6.2), while the effluent in the spring 31 is rather circum-neutral (6-6.6) (for the observed period); all samples from both springs are characterized by elevated concentrations of SO_{4-}, Fe, Ca^{2}_{+} Mg^{2+} and other metals; the content of Ca^{2+} in the springs water is higher than in the mine water; HCO_3^-, lacking in the mine water, are found in the springs effluents in concentrations substantially higher than ones in the clean groundwater.

The increased concentrations of HCO_3^- and Ca^{2+} (in comparison with mine water) can indicate the high rate of calcite dissolution by acidic main drainage. Approximately close concentrations of SO_4^{2-} in samples from the spring 29 and from the Kospashskaya mine suggest that this spring effluents origin from this underground mine. The loading of SO_4^{2-} in the spring 29 is unlikely substantially affected by reactions with the neutral groundwater.

Table 1 *Different parameters of Adsorption kinetics of Hg^{2+} onto SH-MWCNTs/MoS_2 nanohybrid*

Parameter or constituent	Well 5g	Spr. 29	Spr. 31	Mine water
t, C°	4.7	7.03	4.6	8.38
pH	7.8	5.4	6.3	3.5
HCO_3	166.70	320.9*	591.40	0
SO_4	40.00	4863.0	3066.0	4799.0
NH_4	0.04	1.18	0.60	1.55
NO_3	0.17	0.14	0.1	0.1
Ca	35.70	437.59	536.05	332.23
Mg	11.47	462.46	341.835	344.76
Na	2.74	9.36	9.66	7.67
K	0.31	23.80	16.04	41.15
Fe_{tot}	0.09	1904.5	845.2	2888.6
Al	0.01	8.59	1.79	76.99
Mn	0.001	26.993	17.705	37.16
Si	3.42	7.26	7.49	12.68
Calcite ($CaCO_3$)	-0.21	-2.68	-0.53	n.d.
Dolomite ($CaMg(CO_3)_2$)	-0.89	-5.29	-1.21	n.d.
Siderite ($FeCO_3$)	-9.13	-0.09	1.44	n.d.
Rhodochrosite ($MnCO_3$)	-2.34	-1.36	0.49	n.d.
Ferrihydrite [amorphous $Fe(OH)_3$]	2.95	4.13	5.82	1.31
Goethite (FeOOH)	8.07	9.33	10.93	6.60
Amorphous $Al(OH)_3$	-1.52	-1.91	0.68	-5.68
Gibbsite [$Al(OH)_3$]	1.36	0.95	3.57	-2.83
Diaspore (AlOOH)	2.50	2.09	4.70	-1.68
Manganite (MnOOH)	2.52	-4.40	-2.34	-7.30
Gypsum ($CaSO_4$*$2H_2O$)	-2.21	-0.13	0.01	-0.29
Jarosite-K [$KFe_3(SO_4)_2(OH)$]	-4.56	11.73	12.86	8.68
Jarosite-Na [$NaFe_3(SO_4)_2(OH)_6$]	-7.57	7.44	8.72	4.03
Jarosite-H [$(H_3O)Fe_3(SO_4)_2(OH)_6$]	-12.25	5.05	5.00	3.48
Jurbanite [$Al(SO)_4(OH)$*$5H_2O$]	-5.21	0.98	1.36	0.40
Alunite [$KAl_3(SO4)_2(OH)_6$]	-4.86	6.39	10.61	0.14
Basauluminine[$Al_4SO_4(OH)_{10}$*$5H_2O$]	0.87	5.46	14.15	-6.74
log Pco_2	-2.65	-0.51	-0.84	n.d.
n of samples	6	12	10	9

* For Spr. 29, mean value of HCO_3^- was calculated ignoring 4 samples with none HCO_3^-.

In the spring 31, concentrations of SO_4^{2-} are notable lower than in the mine water. That may indicate the greater degree of the mine water neutralization by carbonate minerals of host rocks and neutral groundwater of the coal overlying aquifer (that leads to precipitation of secondary compounds). However, high concentrations of HCO_3^- and Ca^{2+} in the spring effluent may contradict the assumption about the significant dilution of the AMD by ambient groundwater.

Thus, the evaluation of the geochemical data enables us to state that the considered springs discharge the mine effluent that has been neutralized in different degrees by reactions with carbonate minerals, while their interaction with uncontaminated neutral groundwater along the mine flow path is not substantial.

Modeling of mine water − groundwater mixing in different ratio has been conducted to predict the possible composition of the solution resulted in case if the mine water inflows to neutral groundwater. Mean composition of the mine water and the groundwater (well 5g) were taken into account in modeling. Changes of pH values and concentration of HCO_3^-, Fetot and SO_4^{2-} in the solutions obtained by modeling of the mine water and the groundwater mixing are shown in the plots (Fig. 1 a, b). The plot in Fig. 1a indicates that the pH of the resulting solutions reaches the values closed to ones the springs (29 and 31) have only if the dilution ratio of mine water and groundwater mixing is more than 1:9. In case of such dilution, the concentrations of the considered components (HCO_3^-, Fe_{tot} and SO_4^{2-}) turn out to be substantially lower than those measured in both springs (Fig. 1 a, b).

In order to predict a possible composition of neutralized mine water, the modeling of the mine water interaction with calcite was performed. In the modeling, mean chemical composition of the mine water (Table 1) was used. Reactions with calcite were maintained by equilibrium with atmospheric oxygen and gypsum, and calcite. The equilibrium with respect to calcite was assigned from "-6" to "0". Results of the modeling are summarized in the plots (Fig. 2 a, b, c). The plots show the values of pH and concentrations of HCO_3^- and SO_4^{2-}as functions of calcite saturation index (SI). As can be seen in Fig. 2 a, b the measured pH values and concentrations HCO_3^- in the springs samples match or are very close to these values in the modeling solutions, at corresponding SI of calcite. The interaction of AMD with calcite leads to decrease of concentrations of SO_4^{2-}, as it shown in Fig. 2 c. The contents of SO_4^{2-} in spring 31 are close to the ones in the model solutions. The spread of values in the plots is due to the average composition of mine water was taken for modeling.

The modeling of the mine water interaction with calcite has showed that the composition of springs water is mainly caused by dissolution of calcite. The modeling of AMD mixing with clean groundwater and comparison of the results with real water chemistry of the both springs have not revealed any substantial dilution of the mine water by the groundwater (and, consequently, any substantial influence of neutral groundwater on the AMD composition) along the AMD flow path. The results of the simulations confirm the assumption that the considered springs (29 and 31) are the mine effluents which has been subjected to different degrees of neutralization when seeping through carbonate rocks.

It should be noted that, the latest samples taken from spring 29 in September and October 2013 are characterized by low pH values 4.0 and the absence of HCO^{3-}. The decreased pH of water in the spring 29 in 2013 compared with 2011-2012 indicates that the acid neutralizing capacity of carbonate aquifer along the mine water flow path has substantially diminished. It may be caused by coating (armoring) of the limestone surfaces in result of precipitation of $Fe(OH)^3$ and other secondary compounds.

Conclusions

In order to evaluate the processes affecting the neutralization of acid mine drainage when it inflows to karstic carbonate aquifer, modeling of AMD mixing with neutral groundwater, mine water interaction with calcite and SI calculations on the base of the PHREEQC geochemical code were performed. The compositions of the resulting solutions were compared with the actual chemical composition of the springs

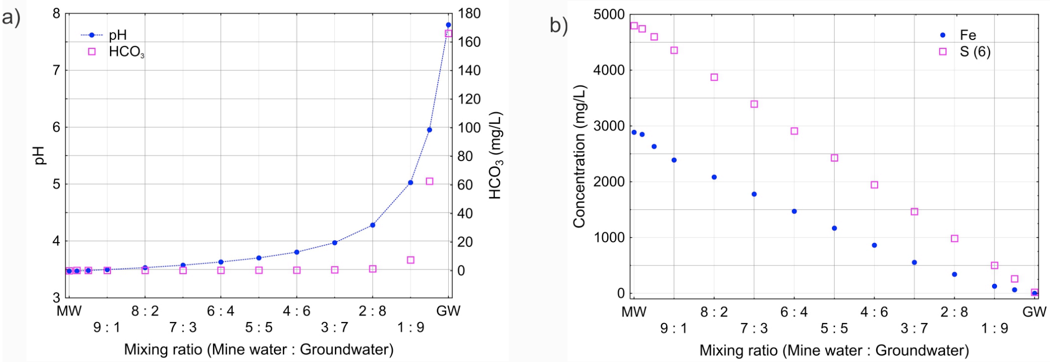

***Figure 1** The results of modeling of acid mine water and clean groundwater mixing*

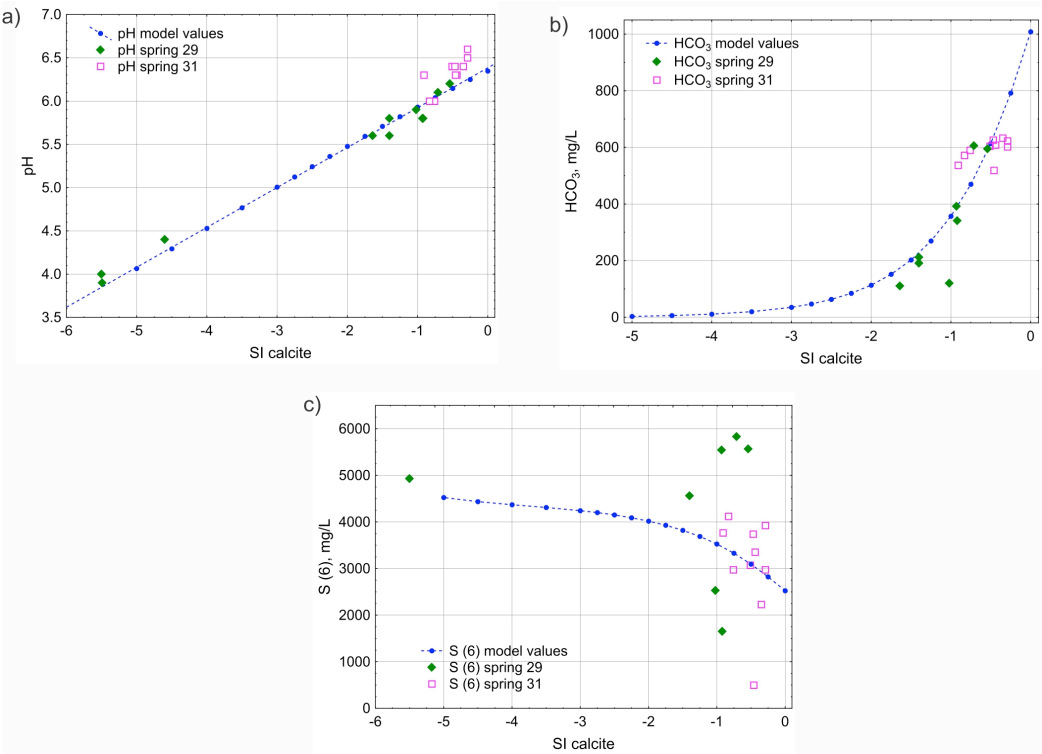

***Figure 2** Modeling of mine water interaction with calcite*

effluents. Comparison of the pH values and HCO_{3-} concentrations in the simulated solutions with measured pH and content of the compounds in the springs water has indicated that chemical composition of the springs (29 and 31) effluents forms mostly due to the dissolution of carbonate minerals of the water-bearing rocks by acidic mine water while dilution of the mine water with neutral groundwater of the deposits (Cv1+s) overlying the coal strata is not significant.

Calculated saturation indexes of water from the springs indicate the potential for precipitation of Fe, Al hydroxides and hydroxysulfates. Saturation indexes of water samples from the spring 29 with respect to AlOH3 are mostly negative (ranges from -7.60 to 0.69), while they are predominantly positive in spring 31 (ranges from -0.49 to 1.28). The SI values of siderite and rhodochrosite are positive in all water samples from the spring 31 and range from negative to positive in the samples from spring 29.

It is particularly remarkable that, the water temperature in the spring 29 (mean 7.03°C) is close to the temperature of the mine waters (mean 8.38°C), while the water temperature in the spring 31 (mean 4.6°C) corresponds to temperature of groundwater of the upper Visean aquifer.

The chemical compositions, saturation state, and the temperature of the springs effluents allow saying that the residence time of the mine water, discharged by the spring 29, within the carbonate flow path is less than those of the mine water discharged by the spring 31. The decrease of pH values in the spring 29 in 2013 in comparison with 2011-2012 is obviously connected with diminish of acid neutralizing capacity of carbonate rocks caused by coating of the limestone surfaces in result of precipitation of secondary compounds along the mine water flow path.

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