

Chemical speciation of pollutants in waters of Dexing Copper Mine area by using chemical equilibrium model-MINTEQA2

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Abstract—The MINTEQ program is used on the speciation of pollutants in waters of Dexing Copper Mine area. Four kinds of waters are encountered. The results show that all pollutants are dissolved phase in typical acid mine drainage, with pH increasing, the iron, aluminum and copper would be precipitated at different pH values. After receiving alkaline wastewater, pH value of the Dawu River water goes higher, resulting in increasing amount of pollutants bounded in solid phase. For the mixed water, the speciation results show that at mixing ratio (alkaline water to acid water) of 8 to 9, neutral water will be gained and different pollutants will precipitate completely at different mixing ratios.

Keywords: chemical speciation; chemical equilibrium model; copper mine.

INTRODUCTION

There are two important kinds of wastewater within the Dexing Copper Mine area. One is the acid mine drainage with pH about 2.3, resulted from the weathering process undergoing the stope and the waste stone dump, the other is the alkaline wastewater which comes from the ore dressing plant and consists of large amount of suspended ore tailings with pH about 12.

In this report, the MINTEQA2 program, a geo-chemical equilibrium model, will be used to evaluate (1) the chemical speciation of pollutants in the wastewaters generated from the mining area in order to give a better understanding of their characteristics, (2) the chemical speciation of the river water before and after mixing with the wastewaters to make a further investigation of the river water quality, and (3) the chemical speciation of the mixed water of acid and alkaline wastes for modeling the neutralization process in order to determine the optimum mixing ratio to maintain some relevant important parameters.

In general, all reactions taking place in the aquatic environment are of kinetic processes, some are fast and some are slow. Actually, it is very difficult to establish a real equilibrium state in natural waters and the equilibrium calculation can only represent a trend towards which the reactions would reach after an immense time of stable processes. Sometimes the determination of trends may have its significance, but in most cases the real situation of a given system can not

be described well by the equilibrium calculation. After all, when using chemical equilibrium models to consider natural waters, one has to make certain assumptions and adjustments in order to minimize errors between the real situation and the calculation results. This problem will be discussed in detail later in this report with considering waters in the mining area.

RELEVANT TO THE MINTEQA2 PROGRAM

There exist many types of mathematical models and corresponding computer softwares which can be used to simulate environmental processes with different objectives and by adopting different methods. The function of a chemical equilibrium model is to calculate equilibrium concentrations of chemical species in an aqueous solution. Typical chemical equilibrium models are series of REDEQL, MICROQL, MINEQL, WATEQ and MINTEQ, and so on, each of which has different versions and can be applied to problems different size and scope.

MINTEQ family of programs, of which the latest version is MINTEQA2, were developed by USEPA with combination of characteristics of MINEQL and WATEQ. MINTEQA2 can model 70 components, more than 500 aqueous complexes, about 400 minerals, 16 gaseous species, and 21 redox couples. In addition, 7 different adsorption algorithms can be used to consider adsorption processes.

Two terms are defined in MINTEQA2 program, namely component and species. The term species is no other than that normally defined in the classical aquatic chemistry, but components, or basis species, are defined as aqueous species that can be used to represent reactants in all reactions to be considered. Only components are used to represent reactants in chemical reactions that generate other species as products and any component can not be represented as a reaction product of any other components.

MINTEQA2 uses chemical equilibrium constant method to relate among species in chemical systems. By incorporating mass conservative law, i. e., mass balance equations, a set of nonlinear equations can be obtained. With Newton-Raphson iteration method as a tool to solve the problem, we can get equilibrium concentrations of individual species in the aqueous solution.

MINTEQA2 incorporates two equations to modify the chemical equilibrium constants for temperature variation. One is a power function with seven empirical constants which are only available for limited number of species, and the other is the Van t Hoff equation which can make temperature correction of the equilibrium constants from 25°C. Correction of activity coefficients can be made by Deby-Huckel equation and the Davies equation.

Seven adsorption algorithms are available in MINTEQA2 for modeling the adsorption of ions on solid surfaces. These include: (1) the activity K_d model, (2) the activity Langmuir model, (3) the activity Freundlich model, (4) the ion exchange model, (5) the constant capacitance model, (6) the triple-layer model, and (7) the diffused double layer model. The first four models neglect the electrostatic influences of charged sorbent surfaces on the nearby solution and the counter influences of changes in sorbent surface charge due to solution composition, and the latter three models are surface complex models which account for the electrostatic effects.

PARAMETERS AND ADSORPTION CONSTANTS

Several types of parameters are needed when MINTEQA2 is used to calculate the equilibrium speciation of a given aqueous solution. These are (1) stoichiometry of components in species, (2) formation constants and enthalpy of species considered, (3) constants needed in correction equations, (4) other relevant information, such as gram formula weights, alkaline factors and (5) parameters for adsorption algorithms.

MINTEQA2 has a large database that contains the first four types of data listed above, but no adsorption parameters. Generally, data in the database can be used safely if no special needs are considered, as they were evaluated very carefully when being added into the database. Nevertheless, they can be changed easily if you do need to re-evaluate them for a particular problem. For problems which involve adsorption processes, parameters for adsorption algorithms have to be added according to simulating experimental results or proper literatures.

As for waters in Dexing Copper Mine areas, it is obviously that adsorption can not be neglected because both alkaline wastewater and Dawu River water contain large amount of suspended solids. The alkaline wastewater from ore dressing plant carries huge amount of suspended ore tailings and the Dawu River water has not only suspended ore tailings but also suspended natural minerals and secondary products of precipitation and coagulation reactions. The adsorption on these solids may have some important effects on the behavior of heavy metals.

The composition of suspended matters in natural waters can be very complex which makes it impossible to consider adsorptions on all individual solids simultaneously. In their report, there is an accounting for the adsorption processes only on suspended ore tailings and $\text{Fe}(\text{OH})_3(\text{am})$ resulted from hydrolytic reactions.

The simulating experiments show that in the problem considered, the adsorption processes can be interpreted by Freundlich model which has the mass action equation



where, K_f^{act} = activity Freundlich adsorption constant

$$K_f^{\text{act}} = \frac{(\text{SOHM}^{m+})}{(M^{m+})^{1/n}}$$

(M^{m+}) = activity of sorbate species in the equilibrium solution, (SOHM^{m+}) = activity of the sorbed complex, and $1/n$ = stoichiometric coefficient of the sorbate.

The experiments simulated the adsorption of Cu^{2+} , Cd^{2+} and Pb^{2+} on both suspended ore tailings and amorphous ferric hydroxide. The results show that the adsorption constants K_f^{act} are pH dependent. Therefore, it is necessary to modify the Freundlich adsorption algorithm to consider pH effect and gain integrated adsorption constants.

Considering the adsorption reaction:



$$K_{ad} = \frac{(\text{SOM})(\text{H}^+)^r}{(\text{M}^{m+})^{1/n}}, \quad (3)$$

where K_{ad} = the integrated adsorption constant, and r = stoichiometric coefficient of H^+ , we can get

$$\log K_f^{\text{act}} = \log K_{ad} + r\text{pH}. \quad (4)$$

This means that if the Reaction (2) could perfectly reflect the real adsorption process, the curve $\log K_f^{\text{act}}$ versus pH would be a straight line with intercept $\log K_{ad}$ and slope r . The calculated results are shown in Table 1.

Table 1 Calculated results of adsorption parameters

Adsorbent	Sorbate	$\log K_{ad}$	r	$1/n$
Ore tailings	Cu^{2+}	-9.85	1.46	0.70
	Cd^{2+}	-10.13	1.22	0.72
	Pb^{2+}	-7.57	1.18	0.80
$\text{Fe}(\text{OH})_3(\text{am})$	Cu^{2+}	-8.46	1.36	0.70
	Cd^{2+}	-9.32	1.34	0.62
	Pb^{2+}	-6.37	1.15	0.58

GENERAL ASSUMPTIONS

As mentioned above, the results of chemical equilibrium calculation can represent absolute equilibrium states, but actually only partial or local equilibriums can be found in nature, especially in heterogeneous systems. Homogeneous liquid phase reactions, however, are much faster than gaseous phase or solid phase reactions and faster than gas-liquid, gas-solid and liquid-solid transfer reactions. Thus, it is reasonable to assume that there exists chemical equilibrium among dissolved species in natural waters when considering no very slow reactions, and no overall equilibrium will be gained when gaseous and solid phases are involved.

As for waters considered in the Dexing Copper Mine area, we should account for both gaseous and solid phases besides liquid phase because acid mine drainage and alkaline wastewater are all resulted from water-atmosphere-mineral contacts and actually large amount of suspended solids exist in both alkaline wastewater and Dawu River water. We should note that waters in the mining area have typical features of mountainous rivers, sufficient contact among gaseous, solid and liquid phases can be obtained due to the great turbulence and mobility of the waters. By this reason, reactions between phases can be fastened and this makes it possible for us to consider equilibrium between solid-liquid and gas-liquid phases.

The gases which can take part in the reactions between atmosphere and aqueous solutions are mainly oxygen and carbon dioxide. Oxygen in waters in the mining area is often saturated, but unfortunately, as oxygen takes part in redox reactions which are often slow processes, it is

hard to say that there exists chemical equilibrium between oxygen and the aqueous solution. As for carbon dioxide, we assume that even though there exists chemical equilibrium between the two phases, the amount that takes part in reactions is negligible. Therefore, it is reasonable to wave aside gaseous phase in the speciation of waters in the mining area.

Another important problem is about redox reactions in waters of the mining area. Generally, redox reactions are often slow processes. Darrell K. Nordstrom and others (1978) investigated redox processes of iron in acid mine drainage. They concluded that in a natural water there existed a typical E_H value but this value is not equilibrated with gases and solids. It was not very successful to use E_H for qualitative purposes. Most measured E_H values could only be used as qualitative means because the measurement and calculation of E_H were constrained by many strict requirements which were not easy to meet with. It was proved that for the acid mine drainage that Darrell, K. Nordstrom and others investigated, the E_H value was controlled by Fe^{2+}/Fe^{3+} rather than O_2/H_2O . In this report measured concentrations of components with different element valences rather than redox equilibrium calculation were used.

Polymerization of Fe^{3+} and Al^{3+} in concentrated solutions played an important role in the speciation of iron and aluminum. Unfortunately, no sufficient data are available for quantitative calculations. Thus no polymerization effects of iron and aluminum are included in this paper.

From the above consideration, the following assumptions in conducting speciation works on waters in Dexing Copper Mine area are made: chemical equilibria of metals between aqueous solution and solid phases are included; atmosphere-solution equilibria, gases as CO_2 and O_2 , redox equilibria and polymerization of iron and aluminum not involved.

SPECIATION OF WATERS IN THE MINING AREA

Acid mine drainage

1. Typical composition of the acid mine drainage

Table 2 Typical composition of the acid mine drainage

Component	t. a. conc. *	Component	t. a. conc. *
Ca^{2+}	6.47×10^{-3}	Cu^{2+}	1.57×10^{-3}
Mg^{2+}	3.38×10^{-2}	Cd^{2+}	1.80×10^{-6}
Na^+	2.20×10^{-4}	Pb^{2+}	9.70×10^{-7}
K^+	8.28×10^{-4}	Zn^{2+}	3.80×10^{-5}
Fe^{3+}	3.95×10^{-2}	SO_4^{2-}	1.28×10^{-1}
Fe^{2+}	1.00×10^{-3}	Cl^-	1.83×10^{-4}
Mn^{2+}	7.30×10^{-4}	F^-	6.80×10^{-4}
Al^{3+}	2.00×10^{-2}	NO_3^-	8.17×10^{-4}
		PO_4^{3-}	3.77×10^{-3}
pH = 2.3			

* Total analytical concentration, mol / L

The typical composition of the acid mine drainage was chosen according to the results of chemical analysis of samples collected in 1987 and 1988. Data listed in Table 2 are not exactly averages of individual measures, for small adjustments were made to make charge balance. In addition, the total amounts of pollutants were converted to the total analytical concentrations of components which were defined in MINTEQA2 and can be inputted directly into the program. For example, the total amount of sulfur in typical acid mine drainage is 4100 ppm and we assume that all sulfur were bounded in species formed from SO_4^{2-} , then we converted the total sulfur into the total analytical concentration of SO_4^{2-} , i. e., 1.28×10^{-1} mol/ L.

2. Calculated results of speciation of main pollutants in typical acid mine drainage

In samples of acid mine drainage, little or no suspended matters were found, so in MINTEQA2 calculations on the acid mine drainage, adsorption processes were not involved.

The speciation results of Fe, S, Cu, Cd and Pb showed that at pH 2.3 which represents the acidity of typical acid mine drainage, no precipitated species was formed. This means that all pollutants in typical acid mine drainage remain as dissolved species.

The speciation of Fe in typical acid mine drainage is : FeSO_4^+ 54.2%, $\text{Fe}(\text{SO}_4)_2^-$ 22.9%, $\text{FeH}_2\text{PO}_4^{2+}$ 9.3%, Fe^{3+} 5.7%, FeOH^{2+} 3.1%, $\text{Fe}_2(\text{OH})_2^{4+}$ 2.4%, and other 2.5%.

The speciation of S in typical and mine drainage is: SO_4^{2-} 40.2%, FeSO_4^+ 19.3%, $\text{Fe}(\text{SO}_4)_2^-$ 16.2%, $\text{MgSO}_4(\text{aq})$ 11.9%, $\text{Al}(\text{SO}_4)_2^-$ 4.1%, HSO_4^- 4.1% and other 4.4%.

There are two species formed from Cu^{2+} , namely $\text{CuSO}_4(\text{aq})$ and Cu^{2+} , and the concentration of free Cu^{2+} (56.7%) is a little higher than that of SO_4^{2-} (43.3%) bounded species. Cd can be in species Cd^{2+} , $\text{CdSO}_4(\text{aq})$ and $\text{Cd}(\text{SO}_4)_2^{2-}$, with percentage of the total to be about 40%, 40% and 20%, respectively. Similarly the dominant species of Pb is PbSO_4 [$\text{PbSO}_4(\text{aq})$ 56.8%, Pb^{2+} 29.0% and $\text{Pb}(\text{SO}_4)_2^{2-}$ 14.2%].

3. Speciation of typical acid mine drainage at different pH

Fixing pH values at 2.0 through 6.0 with step of 0.5 pH units, calculations can represent titration process of the acid mine drainage by strong base.

Fig. 1 represents precipitated percentages of Fe, Al, Cu and S pollutants as functions of pH. It indicates that precipitated iron can be formed at pH greater than 2.5 and precipitation finished at pH 4.0. The precipitated species of iron is ferric hydroxide ($\text{Fe}(\text{OH})_3$) at pH below 4.5 and transferred into magferrite (MgFe_2O_4) as pH increasing above pH 5.0. Aluminum also precipitates at pH greater than 2.5 but the curve of its precipitation percentage versus pH values locates 0.5 pH units right to that of iron and the shape of the two curves are similar. The precipitated aluminum is in alunite ($3\text{Al}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$) at pH lower than 4.0 and in diaspor

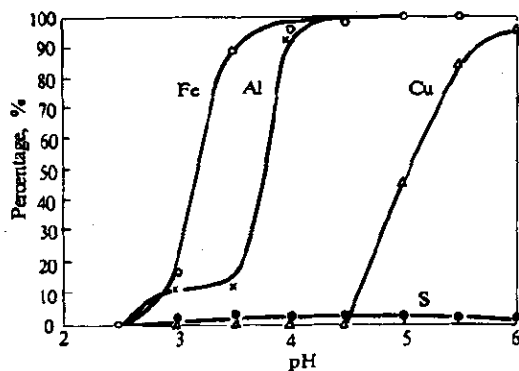


Fig. 1 Precipitated percentage of pollutants in typical acid mine drainage

(AlOOH) at pH greater than 4.5 Copper precipitates in $\text{Cu}_3(\text{PO}_4)_2$ at pH greater than 4.5 and finishes precipitation at pH above 6.0. Changing of pH has little effects on the precipitation of pollutant sulfur and the percentage of its precipitation is negligible.

Speciation of heavy metal pollutants in the acid mine drainage at different pH values shows that as pH increases, the concentrations of Cu^{2+} , Cd^{2+} and Pb^{2+} decrease and the total amounts of SO_4^{2-} bounded complexes increase.

Alkaline wastewater

1. Typical composition of the alkaline wastewater

Table 3 lists the typical composition of the alkaline wastewater and was generated similarly to Table 2.

2. Speciation of alkaline wastewater with typical composition

The result of MINTEQA2 calculation on typical alkaline wastewater shows that nearly all of iron and copper is precipitated but sulfur remains dissolved. And 82.2% of Cd is in precipitated species and 17.8% is adsorbed on the surface of suspended solids. The equilibrated mass distribution of some main pollutants in alkaline wastewater are given in Table 4.

Table 3 Typical composition of the alkaline wastewater

Component	t. a. conc. *	Component	t. a. conc. *
Ca^{2+}	5.13×10^{-3}	Cu^{2+}	4.88×10^6
Mg^{2+}	5.31×10^{-3}	Cd^{2+}	5.34×10^{-7}
Na^+	7.61×10^{-3}	SO_4^{2-}	1.00×10^{-3}
K^+	5.05×10^{-3}	HS^-	1.00×10^{-3}
Fe^{3+}	1.00×10^{-3}	Cl^-	1.47×10^{-4}
Mn^{2+}	4.19×10^{-6}	NO_3^-	7.74×10^{-5}
Al^{3+}	1.12×10^{-4}	F^-	1.58×10^{-5}
		CO_3^{2-}	5.00×10^{-3}

pH = 12

* Total analytical concentration, mol / L

3. Speciation of alkaline wastewater at different pH

MINTEQA2 executions on the alkaline wastewater with typical composition were conducted at pH 7 to 12. The results show that the mass distribution of main pollutants in dissolved, sorbed, and precipitated phases could be approximately regarded to be unchanged at pH 7 to 12. As most of main pollutants are in suspended solid phase and the total amounts of

Table 4 Mass distribution of main pollutants in the alkaline wastewater

Component	Dissolved		Sorbed		Precipitated	
	mol/ L	%	mol/ L	%	mol/ L	%
Fe^{3+}	2.0×10^{-10}	0.0	0.0	0.0	1.0×10^{-3}	100.0
Al^{3+}	6.3×10^{-5}	55.9	0.0	0.0	4.9×10^{-5}	44.1
Cu^{2+}	0.0	0.0	0.0	0.0	4.9×10^{-6}	100.0
Cd^{2+}	0.0	0.0	9.5×10^{-8}	17.8	4.4×10^{-7}	82.2
SO_4^{2-}	1.0×10^{-3}	100.0	0.0	0.0	0.0	0.0
HS^-	1.0×10^{-3}	99.5	0.0	0.0	5.3×10^{-6}	0.5

dissolved species are negligible, the speciation of the dissolved species will be of little help to us. With this consideration, detailed speciation results are not presented.

Dawu River water

1. The chemical composition of the river water

Three typical sections of the river were chosen for chemical speciation calculation, representing waters before receiving alkaline wastewater, after receiving alkaline wastewater and before entering into Le An River. The compositions of waters at the three sections are listed in Table 5.

2. MINTQA2 calculation on Dawu River water

The results on speciation of Dawu River based upon data listed in Table 5 are briefly given in Fig. 2-6. It is shown that after receiving alkaline wastewater, pH of the river water increases, resulting in increasing amounts of precipitated and sorbed species. At section 2 and 3, repre-

Table 5 Chemical composition of Dawu River water for speciation calculation, mol / L

Component	Section 1	Section 2	Section 3
Fe ³⁺	1.7×10^{-3}	8.0×10^{-4}	3.7×10^{-4}
Mn ²⁺	1.0×10^{-4}	3.0×10^{-4}	8.2×10^{-5}
Al ³⁺	2.5×10^{-3}	8.0×10^{-4}	6.3×10^{-4}
Cu ²⁺	1.8×10^{-4}	8.2×10^{-5}	6.7×10^{-5}
Cd ²⁺	5.0×10^{-7}	3.0×10^{-7}	3.0×10^{-7}
Pb ²⁺	1.0×10^{-6}	5.5×10^{-7}	3.4×10^{-7}
Zn ²⁺	2.4×10^{-5}	1.0×10^{-5}	1.0×10^{-5}
Ca ²⁺	2.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}
Mg ²⁺	2.8×10^{-3}	1.0×10^{-3}	1.0×10^{-3}
Na ²⁺	5.0×10^{-4}	5.0×10^{-4}	5.0×10^{-4}
K ⁺	1.4×10^{-3}	1.0×10^{-3}	1.0×10^{-3}
SO ₄ ²⁻	1.1×10^{-2}	5.3×10^{-3}	5.3×10^{-3}
PO ₄ ³⁻	1.8×10^{-5}	2.5×10^{-5}	2.5×10^{-5}
NO ₃ ⁻	8.5×10^{-5}	8.5×10^{-5}	3.7×10^{-5}
Cl ⁻	9.3×10^{-5}	9.3×10^{-5}	9.3×10^{-5}
pH	3.1	4.5	5.2

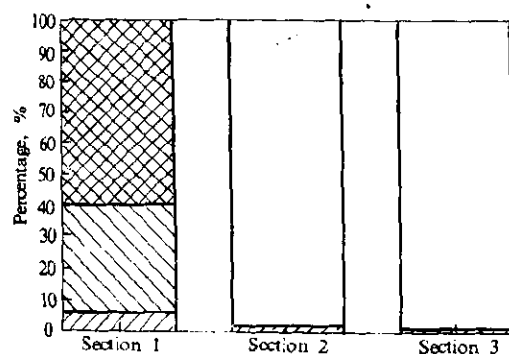


Fig. 2 Speciation of Fe in Dawu River

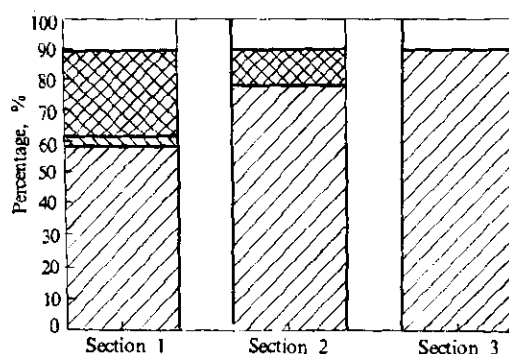


Fig. 3 Speciation of S in Dawu River

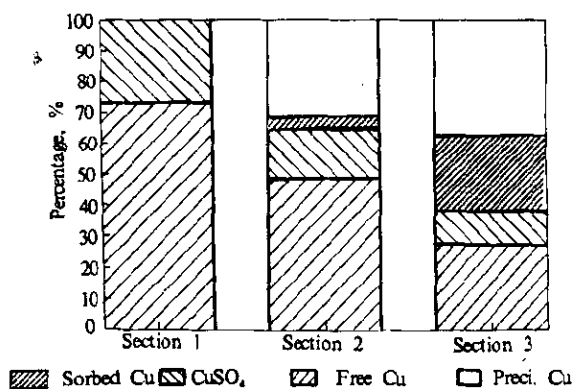


Fig. 4 Speciation of Cu in Dawu River

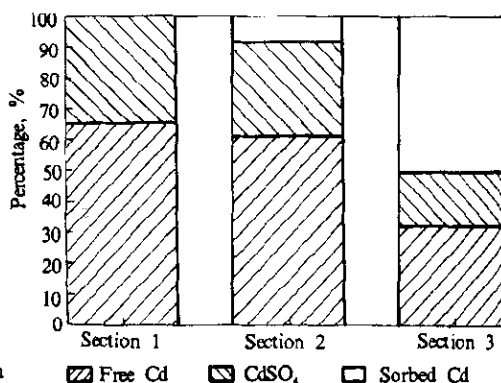


Fig. 5 Speciation of Cd in Dawu River

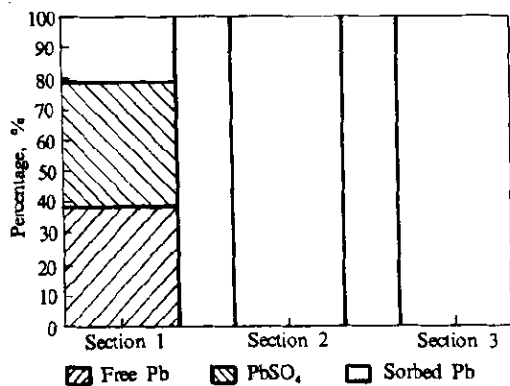


Fig. 6 Speciation of Pb in Dawu River

Mixed water

Characteristics of the water resulted from the mixing of acid mine drainage with alkaline wastewater was evaluated, using data in Table 2 and 3 as compositions of the two wastes.

Fig. 7 gives the curve of pH values of the mixed waters versus different mixing ratios of alkaline wastewater to acid mine drainage. It indicates that at mixing ratio of 8 to 9, the mixed water will become neutral. Fig. 8 shows that at mixing ratio of 6, total iron will be precipitated and copper will finish precipitation at about mixing ratio of 2 and, cadmium and lead will be precipitated completely at mixing ratio of 4.

SUMMARY AND SUGGESTIONS

In this report, the MINTEQA2 program was used for chemical speciation of pollutants

senting river waters after receiving alkaline wastewater and before entering into Le An River, nearly total amount of iron is in suspended mineral phase. The dominant precipitated species of iron at section 2 is ferric hydroxide ($\text{Fe}(\text{OH})_3$) and at section 3 it is transferred into mag-ferrite (MgFe_2O_4). This indicates that the content of iron in downstream river water is mainly controlled by physical processes. Sulfur mainly exists as SO_4^{2-} and transported downstream in the river. Copper and cadmium remains in dissolved phase at section 1 but become partially sorbed and precipitated at section 2 and section 3, the precipitated species of copper is mainly covellite (CuS).

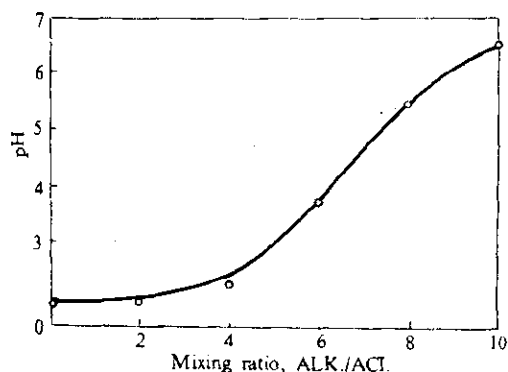


Fig. 7 pH variation in the mixed water with different mixing ratios

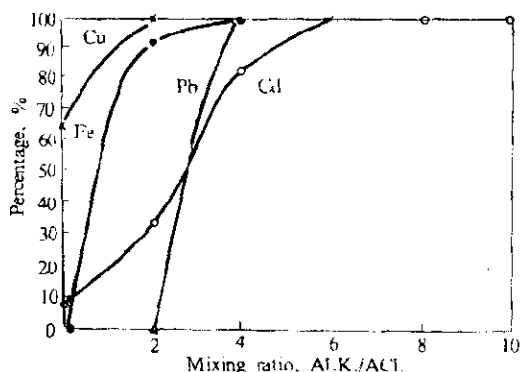


Fig. 8 Precipitation percentage of pollutants in the mixed water with different mixing ratio

in waters of Dexing Copper Mine area, involving four kinds of waters: (1) the acid mine drainage, (2) the alkaline wastewater, (3) the Dawu River water, and (4) the water resulted from the mixing of acid mine drainage with alkaline wastewater. The calculated results and the experimental results were tallied well, indicating that the assumptions made above are rather reasonable.

After receiving alkaline wastewater, pH value of the Dawu River water goes higher, resulting in increasing amount of pollutants bounded in solid phase. For the mixed water at mixing ratio of 8 to 9, neutral water will be gained and different pollutants will precipitate completely at different mixing ratios.

As chemical equilibrium models can only describe absolute equilibrium state of an aqueous solution, further investigations have to be made on the kinetic behavior of main chemical processes undergoing in natural waters and the assumptions have to be evaluated carefully.

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