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Araştırma Makalesi/Research Article

Destruction of Sodium Cyanide and Determination of Hydrogen Index of the Industrial Waste Water

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Abstract. Currently, cyanide leaching technologies of gold were widely adopted in existing and projected gold mining plants, where during the running wastewater with complex composition and toxic components are formed. Accordingly, pulp after sorption cyanidation process become off-line moldboard and must be disposed. At the same time in world practice the process of cyanide oxidation by mixture of sulfur dioxide and air is very widespread. As a donor of SO_2 sodium metabisulphite ($Na_2S_2O_5$) is the most commonly used. The chemistry of this process is quite complex and consists of multi-stages and little-studied. Taking into account the above positions, in this study physical, chemical modeling of the interaction of sodium cyanide with sulfur dioxide and sodium metabisulfite in oxygen-water system with catalyst was carried out. The equations of chemical reactions were given and the basic matrices of physical, chemical modeling of the studied technological process were defined. The chemistry of transition process of cyanides in to metal cyanides using sodium metabisulfite was determined. The equilibrium composition, pH value, electrode potential, ionic strength of solution were calculated. And also were calculated spectra of concentration distribution of the individual components in the phases at water temperatures (T = 278 K)

Keywords: Distribution; Sodium cyanide; Sodium Metabisulfite; Sulfur dioxide.

Endüstriyel Atık Sulardaki Sodyum Siyanürün Tahrip Edilmesi ve Hidrojen Değerinin Belirlenmesi

Özet: Şu anda, altının siyanürleme teknolojileri mevcut olan ve projelenen madencilik işlerinde geniş kullanılmaktadır. Böyle işlemeler sonucunda karmaşık bir bileşimli ve toksik maddeleri içeren atık sular meydana gelir. Bu duruma göre palp (pulp) sorpsiyon siyanürlemesi sonucunda atık olarak sayılır ve bertaraf edilmesi gerekir. Aynı zamanda kükürt dioksiti ve hava karışımı ile siyanür oksidasyon süreci dünyada yaygındır. SO_2 donörü olarak sodyum metabisülfit ($Na_2S_2O_5$) geniş kullanılır. Bu sürecin kimyası oldukça karmaşıktır, çok aşamadan oluşur ve az incelenmiş. Yukarıda anılanları hesaba alarak çalışmada sodyum siyanürün kükürt dioksit ve sodyum metabisülfiti ile oksijen-su sisteminde katalizörün katılımında etkileşimlerinin fiziksel, kimyasal modellemesi yapılmıştır. Kimyasal reaksiyonların denklemleri sunulmuş ve araştırılan teknolojik sürecin fiziksel, kimyasal modellemesinin temel matrisleri tespit edilmiştir. Siyanürün sodyum metabisülfitinin kullanımında metalik siyanüre geçme işleminin kimyası belirlenmiştir. Çözeltinin denge bileşimi, pH değeri, elektrot potansiyeli, iyonik kuvveti hesaplanmış ve suyun 278K sıcaklığında fazlardaki tek tek bileşenlerin konsantrasyonlarının dağılım spektrumları sunulmuştur.

Anahtar Kelimeler: Dağıtım; Kükürt dioksit; Sodyum metabisülfit; Sodyum siyanür.

Introduction

Currently, the process of cyanide oxidation by mixture of sulfur dioxide and air is very widespread in the world practice (process INCO). As a donor of SO_2 sodium metabisulphite ($Na_2S_2O_5$) has the most commonly used. The chemistry of this process is quite complex and consists of multi-stages and little-studied. Taking into account the above positions, in this study physical and chemical modeling of the interaction of sodium cyanide with sulfur dioxide and sodium metabisulfite in oxygen-water system with catalyst was carried out.

Materials and methods

Formation of the physical and chemical model of process, implemented by the search of potentially possible phases in equilibrium, dependent components and composition of system by independent components at minimum isobaric and isothermic potential in phases (Holland et al. 1990), (Karpov et al., 1988), (Lee-Kesler et al., 1981). In order to calculate thermodynamics of process, possible molecular and ionic equations of chemical reactions were composed, molar ratio of components was found ($Na: C: N: Cu: S: N: O$) in solution, and the structural matrix of the studied system was determined; a lot of analytical work on the preparation of initial data of the thermodynamic functions was done. Research results allowed us:

- to calculate the thermodynamic parameters of the system;
- to determine the equilibrium composition, pH, Eh, ionic strength (I) of solution;
- and set the range of the concentration distribution of the individual components in the (liquid, gas, solid) phases at 278K (5 ° C) and P = 10^5 Pa (1 bar).

These data (temperature and atmospheric pressure) are same with condition in gold factory in the mountains.

Results and discussion

SO_2 oxidation processes were studied in order to reveal the chemistry of internal molecular transformations of substrates, as they can be used to develop methods for decontamination of wastewater from toxic ingredient of metallurgical plants (Carter, 1997), (Chase, 1985), (Koksal, 2002), (Veillette, 1995).

Based on the analysis of sodium cyanide, free cyanide ions such as $(CN)_2$, sodium metabisulfite, sodium hydroxide, oxygen, sulfur dioxide, water and copper sulfate elementary interaction reactions, the total conversion reactions of cyanide ions (CN^-) into a metal cyanates (NCO^-) and insoluble copper cyanide were made. Chemistry of process (I) were established and for the first time chemical and structural matrix of multicomponent heterogeneous systems such as: $Na{:}C{:}N{:}S{:}Cu{:}O{:}H=26{:}22{:}22{:}12{:}8{:}68{:}36$ were composed by working scheme (I) and content of oxygen (68 *mol*) in the system were determined (Table 1-3):

(I) $7H_2O + 7NaCN + 4CuSO_4 + 2(CN)_2 + 4NaOH + Na_2S_2O_5 + O_2 \rightarrow H_2SO_3 + 5Na_2SO_4 + 4CuCN \downarrow + 2(NH_4)_2C_2O_4 + 3NaCNO.$

The equilibrium compositions of the water solution were calculated and the concentration of charged particles (cations and anions) and molecules: Cu^{+1}, Cu^{+2}, $CuOH^+$, HCO_3^-, HS_2O^{3-}, NH_4^+, $NaOH^*$, SCN^-, SO_3^{-2}, SO_4^{-2}, CO_2^*, CO_3^{-2}, HSO_3^-, N_2^*, NH_3^*, NH_4^+, Na^+, SCN^-, SO_3^{-2}, OH^-, H^+, H_2O witch formed in the solution due to the redox process of the initial product were found (Table 4, 6).

The equilibrium composition of the gas phase (NH_3, CO_2, $(CN)_2$, O_2, CH_4, H_2S, HCN, SO_2) was calculated and trace amounts of free cyanide ions, such as $(CN)_2$ (partial pressure 3.79 10^{-44} Pa), HCN 3.17 10^{-21} were found. In fact, these components are in the gas phase practically should be absent.

The formation of the final products such as: NH_3, CO_2, H_2O in the system due to formation and decomposition of sodium cyanate ($NaNCO + 2H_2O \rightarrow NH_3\uparrow + NaHCO_3$, $2NH_3 + H_2SO_4 \rightarrow$

$(NH_4)_2SO_4$, $NaHCO_3 \rightarrow NaOH + CO_2\uparrow$) were determined. These gas components were distributed in gas and liquid medium, depending on their solubility and changing the equilibrium and operating concentration in certain phases.

Physico-chemical simulation process of INCO at 278 K and P = 10^5 Pa

Table 1. Physical Parameters

Temperature, *K*	278	**G, *MJ***	-8.45	**Eh, *B***	-0.424
Pressure, *MPa*	0.1	**H, *MJ***	-9.53	**pe**	-7.70
Volume, m^3	0.197	**S, *kJ/K***	3.27	**pH**	11.231
Mass, *kg*	1.496	**U, *MJ***	-9.54	**Ion strength**	2.803
Density, kg/m^3	7.59	**Cp, *kJ***	2.64	**TDS, mg/kg sol**	71.807

Table 2. Phase Parameters

Name phase	Volume, m^3	Mole quantity	Mass, kg	Density, kg/m^3	Weight %
AqueousSol.	0.000159	6.14e+00	0.153	964.86	10.24
Gas	0.19699	8.61e+00	0.275	1.40	18.45
$Cu(OH)_2$	0.0	6.54e-01	0.063	0.0e+00	4.26
CuCN	0.0	3.35e+00	0.299	0.0e+00	20.04
***Na*-sulphate**	0.0	4.95e+00	0.703	0.0e+00	47.01

Table 3. Independent Components

Components	Chemical composition	Disparity balance mass	Molality	mg/kg sol	Dual solution	Chemical potential	Log molality
Na	10.0	2.45e-09	9.15e-01	2.10e+04	-94.40	-52178	-0.04
C	11.0	8.39e-10	8.32e-01	9.99e+03	8.55	4727	-0.08
N	11.0	1.32e-09	7.14e+01	1.00e+06	6.74	3723	1.85
S	6.0	1.18e-09	1.59e-03	5.12e+01	0.18	101	-2.796
Cu	4.0	6.64e-10	4.47e-04	2.84e+01	33.55	18545	-3.35
H	21.0	1.51e-09	7.51e-01	7.57e+02	-7.47	-4126	-0.12
O	32.0	5.50e-09	2.50e+00	4.00e+04	-89.33	-49374	0.398

Table 4. Dependent Components

Components	gT, MJ/mole	Mole quantity	mg/kg sol or wt.%	Log mole	Coeff. activity	Log cf. activ.	Ln activity
			Gas				
NH_3	-0.036	2.80e-04	0.00	-3.55	1.00	0.000	-10.33
CO_2	-0.393	2.13e+00	33.94	0.33	0.99	-0.003	-1.41
CH_4	-0.049	3.32e+00	19.28	0.52	0.998	-0.001	-0.96
H_2S	-0.034	1.05e+00	12.96	0.02	1.00	0.000	-2.11
			Solid				
$Cu(OH)_2$	-0.370	6.54e-01	5.98	-0.19	1.00	0.000	0.000
CuCN	0.113	3.35e+00	28.10	0.53	1.00	0.000	0.000
Na_2SO_4	-1.263	4.95e+00	65.93	0.695	1.00	0.000	0.000

Na_2SO_4, $Cu\ (OH)_2$, *CuCN* components were detected in the solid phase. The copper cyanide (*CuCN*) precipitated, i.e. cyanides transformed into sodium cyanide (*NaCNO*) and insolubilizing form of copper cyanide (*CuCN*). Thereby while the sodium cyanide decompose, ammonia and carbon dioxide is forming. The pHs of the solution were set in several temperatures. At 298 *K* pH was 9.9967; at 293 *K* pH was 10.2353; at 288 *K* pH was 10.4858; at 283 *K* pH was 10.7467 and at *278 K* pH was 11.0190, i.e. the pH changed from 9.99 to 11.02 in the range of temperature change from 298 *K* to 278 *K*. This implies that cyanides transformed insolubilization form as copper cyanide and sodium cyanat, where sodium cyanat decompose to NH_3 and CO_2 only in an alkaline medium.

Adequacy of the proposed structural model established on the basis of drawing up a mass balance of incoming elements in the system, as well as the balance of the weight percentage of the individual phases (Table 2). Physical and chemical model of the transformation process of cyanide into cyanate metals by using sodium metabisulfite and sulfur dioxide with catalyst and with oxygen in air allowed for the first time to predict the formation of various active particles (cations, anions), molecules and condensed substances in separate phases. And also, absence of free type cyanides $(CN)_2$ was established in gas phase.

Table 5. Dependent Components

Components	gT, MJ/mole	Molality	Mole quantity	mg/kg sol or wt.%	log mole	Coeff. activity	Log cf. activ.	Ln activity
				Aqueous Sol.				
Cu^{+}	0.037	4.47e-04	4.79e-05	2.84e-02	-3.35	0.9	-0.05	-11.88
Cu^{+2}	-0.004	3.74e-14	4.01e-15	2.388e-12	-13.43	0.8	-0.097	-35.19
$CuOH^{+}$	-0.187	4.81e-13	5.15e-14	3.87e-11	-12.32	1.8	0.25	-31.84
HCO_3^{-}	-0.576	7.47e-01	8.01e-02	4.56e+01	-0.13	10.9	1.04	-1.95
HS_2O_{3-}	-0.595	1.17e-14	1.26e-15	1.33e-12	-13.93	8.1	0.91	-34.04
NH_4^{+}	-0.095	2.53e-04	2.71e-05	4.56e-03	-3.598	0.4	-0.37	-13.18
$Na+$	-0.259	4.58e-01	4.91e-02	1.05e+01	-0.34	0.7	-0.13	-5.13
$NaOH*$	-0.442	2.17e-06	2.33e-07	8.68e-05	-5.66	1.7	0.22	-16.58
SCN^{-}	0.077	8.00e-06	8.58e-07	4.65e-04	-5.097	6.8	0.83	-13.87
SO_3^{-2}	-0.537	3.39e-13	3.63e-14	2.71e-11	-12.47	197	2.295	-27.48
SO_4^{-2}	-0.744	1.59e-03	1.70e-04	1.52e-01	-2.80	120	2.08	-5.72
CO_2*	-0.393	1.72e-03	1.85e-04	7.58e-02	-2.76	1.7	0.23	-9.87
CO_3^{-2}	-0.518	8.30e-02	8.90e-03	4.98e+00	-1.08	250	2.39	-1.04
HSO_3^{-}	-0.596	1.43e-15	1.53e-16	1.16e-13	-14.85	7.1	0.85	-36.27
N_2*	0.031	3.57e+01	3.83e+00	1.00e+00	1.55	0.7	-0.18	-0.88
NH_3*	-0.036	7.79e-04	8.35e-05	1.33e-02	-3.11	1.6	0.196	-10.75
OH^{-}	-0.183	9.21e-08	9.88e-09	1.57e-06	-7.04	34.1	1.53	-16.72
H^{+}	-0.058	7.39e-12	7.92e-13	7.45e-12	-11.13	0.3	-0.55	-30.94
H_2O	-0.241	1.98e+01	2.12e+00	3.83e+01	1.297	1.0	0.00	-1.06

Table 6. Gases Parameters

Components	Fugacity	Log fugacity	Partial pressure, Pa	Log partial pressure	Log coeff. fugacity	Coeff. fugacity
NH_3	3.25e-05	-4.49e+00	3.25e-05	-4.49e+00	0.00e+00	1.00
CO_2	2.45e-01	-6.10e-01	2.47e-01	-6.07e-01	-2.79e-03	0.99
$(CN)_2$	3.71e-44	-4.34e+01	3.79e-44	-4.34e+01	-8.77e-03	0.98
O_2	1.00e-70	-7.84e+01	1.00e-70	-7.84e+01	-3.80e-04	0.999
CH_4	3.84e-01	-4.15e-01	3.85e-01	-4.15e-01	-9.42e-04	0.998
H_2S	1.22e-01	-9.14e-01	1.22e-01	-9.14e-01	0.00e+00	1.00
HCN	3.17e-21	-2.05e+01	3.17e-21	-2.05e+01	0.00e+00	1.00
Na_2SO_4	4.13e-56	-5.54e+01	4.13e-56	-5.54e+01	0.00e+00	1.00
$NaCN$	2.68e-48	-4.76e+01	2.68e-48	-4.76e+01	0.00e+00	1.00
SO_2	8.42e-23	-2.21e+01	8.59e-23	-2.21e+01	-8.62e-03	0.98

Thus composed physicochemical model adequately describes the course of the process INCO and accordingly disclose the function of sodium metabisulfite, oxygen in solution, and as well as sulfurous acid as the reaction product of sulfur dioxide and water at 278 *K* temperature and $P = 10^5$ *Pa* pressure.

Symbols

A(T,V)-Helmholtz potential; Cp-specific heat capacity (equilibrium); Eh-electrode potential, V; f- activity ratio; G(T,P) - Gibbs potential; G- Gibbs energy, *J*; g- weight, %; H(S,P) - isobaric and isentropic potential; H-enthalpy, *J*; INCO - sulfur dioxide oxidation method of cyanide by using a copper catalyst; I- ionic strength of the solution; pH-hydrogen ion exponent; P - pressure, *MPa*; pe - logarithm of the concentration of electrons in the solution; S(H,P) -isobaric and isenthalpic potential; S(U,V)- isochoric and isoenergetic potential; S- entropy, *J l/K*; T, t, - temperature, *K*; U- internal energy, J; U(S,V)-isochoric and isentropic potential; V- volume, m^3; l, g, s - liquid, gas and solid phase.

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