CHEMISTRY AND CHEMICAL ENGINEERING

Volume 2020 | Number 1 Article 10

March 2020

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Rosilov Mansur
Tashkent Chemical Technological Institute, rosilovm@mail.ru

Deng Tianlong
Tianjin University of Science and Technology, tldeng@tust.edu

Usmanov Ilham
Tashkent Chemical Technological Institute, ift2015@mail.ru

Samadiy Murodjon
Tashkent Chemical Technological Institute, Tianjin University of Science and Technology, samadiy@inbox.ru

RESEARCH OF KINETIC CHARACTERISTICS OF THE PROCESS OF DECOMPOSITION OF ZINC CONCENTRATE WITH HYDROCHLORIC ACID

Mansur ROSILOV[1] (rosilovm@mail.ru), Tianlong DENG [2] (tldeng@tust.edu), Ilham USMANOV[1] (ift2015@mail.ru), Murodjon SAMADIY[1,2] (samadiy@inbox.ru)
[1]Tashkent Chemical Technological Institute, Tashkent, Uzbekistan
[2]Tianjin University of Science and Technology, Tianjin, China

The aim of the study was the theoretical justification of the kinetic characteristics of the process of producing zinc chloride from zinc concentrate of the Khandiza deposit. For this, the effect of temperature and duration of the process of autoclave zinc extraction in a 28% hydrochloric acid solution was studied at a ratio of Zn: HCI = 1:1.1. Variable parameters were the temperature of 70, 80 and 90 °C and the duration of the leaching process of 6, 8 and 10 hours. The optimal parameters for the production of zinc chloride were determined.

Keywords: zinc concentrate, kinetic characteristics, zinc chloride, reaction rate, Arrhenius equation

ИССЛЕДОВАНИЕ КИНЕТИЧЕСКИХ ХАРАКТЕРИСТИК ПРОЦЕССА РАЗЛОЖЕНИЯ ЦИНКОВОГО КОНЦЕНТРАТА СОЛЯНОЙ КИСЛОТОЙ

Мансур Сиргиевич РОСИЛОВ[1] (rosilovm@mail.ru), Тианлонг ДЕНГ[2] (tldeng@tust.edu), Ильхам Икрамович УСМАНОВ[1] (ift2015@mail.ru), Муроджон Абдусалимзода САМАДИЙ [1,2] (samadiy@inbox.ru)
[1]Ташкентский химико-технологический институт, Ташкент, Узбекистан
[2]Тяньцзинский университет науки и техники, Тяньцзинь, Китай

Целью исследования являлось теоретическое обоснование кинетических характеристик процесса получения хлористого цинка из цинкового концентрата месторождения Хандиза. Для этого рассчитано влияние температуры и продолжительности процесса автоклавного извлечения цинка 28% раствором соляной кислоты при соотношении Zn:HCI=1:1,1. Переменными параметрами были температура 70, 80 и 90 °С и продолжительность процесса выщелачивания 6, 8 и 10 часов. Определены оптимальные параметры получения хлористого цинка.

Ключевые слова: цинковый концентрат, кинетические характеристики, хлористый цинк, скорость реакции, уравнение Аррениуса

RUX KONSENTRATINI XLORID KISLOTASI BILAN PARCHALASH JARAYONINING KINETIK XARAKTERISTIKASI TADQIQOTI

Mansur Sirgievich ROSILOV[1] (rosilovm@mail.ru), Tianlong DENG[2] (tldeng@tust.edu), Ilham Ikramovich USMANOV[1] (ift2015@mail.ru), Murodjon Abdusalimzoda SAMADIY[1,2] (samadiy@inbox.ru)
[1]Toshkent kimyo texnologiya instituti, Toshkent, O'zbekiston
[2]Tianjin Fan va Texnologiya Universiteti, Tianjin, Xitoy

Tadqiqot maqsadi Xandiza koni ruxtutgan konsentratidan rux xlorid olish jarayoni kinetic xarakteristikasini nazariy asoslashdan iborat. Buning uchun Zn:HCI=1:1,1 nisbatda 28% xlorid kislotasi eritmasiga avtoklav usulida ruxni ajratishda xarorat va jarayonning davomiyligini ta'siri urganilgan. O'zgaruvchan parametrlar farqi xarorat 70, 80 u 90 °C va ajratib olish jarayoni davomiyligi 6, 8 va 10 soatni tashkil etdi. Rux xloridi olishning optimal parametrlari aniqlangan.

Kalit so'zlar: rux konsentrati, kinetic xarakteristika, rux xlorid, reaksiya tezligi, Arrinius tenglamasi

Introduction

Zinc chloride is also called zinc chloride and zinc dichloride. This chemical reagent has a fairly wide range of applications. Zinc chloride ($ZnCl_2$) is a white crystals or flakes, sometimes with a yellowish tint, capable of absorbing water vapor from the environment.

Known works on the extraction of zinc and lead by combined, sequential biooxidation and acid leaching of saline from crude complex sulfide ores containing sphalerite, pyrite and galena [1]. As a rule, raw complex lead-zinc sulfide ores cannot be processed by existing metallurgical plants for economic reasons. Even when it is technically possible, difficulties arise due to emissions of gases, especially sulfur dioxide, and vapors during firing and smelting operations. Hydrometallurgical methods for the extraction of metals from sulfides are widely recognized as simple, economical and environmentally acceptable. They are aimed at leaching under pressure [2, 3], chemical leaching [4, 5, 6, 7, 8], bioleaching [9].

The biooxidation of complex zinc-lead sulfides has been extensively studied using samples of sulfide concentrate, pure galena or sphalerite [10, 11, 12]. Among the bacteria involved in leaching, Thiobacillus ferrooxidans has been studied in most detail and is most effective in commercial operations for lead-zinc sulfides [13]. However, some studies have examined the use of Thiobacillus ferrooxidans for the oxidation of complex crude zinc-lead-sulfide ores [14].

These studies were designed to study the hydrometallurgical method for extracting zinc and lead from untreated, complex sulfide ores containing pyrite, sphalerite and galena in Sichuan, China. Since lead remains as insoluble sulfate in bioleaching residues, a process based on the sodium chloride acid system has been developed for lead extraction.

Materials and methods

Zinc was determined by x-ray fluorescence method [15, 16]. The method is based on the collection and subsequent analysis of the spectrum arising from the irradiation of the test material with x-ray radiation - this is a fast, non-destructive and environmentally friendly analysis method with high accuracy and reproducibility of the results. The method allows to qualitatively, semi-quantitatively and quantitatively determining all elements from beryllium to uranium that are in powder, solid and liquid

Таблица 1

Effect of temperature and duration of the leaching of zinc from zinc concentrate

№	Time, hour	Degree of extraction, %		
		70 °C	80 °C	90 °C
1	0	0	0	0
2	1	14,37	14,80	14,94
3	2	27,18	28,00	28,28
4	3	38,45	39,60	39,99
5	4	48,55	50,00	50,50
6	5	57,87	59,60	60,18
7	6	66,23	68,20	68,78
8	7	74,00	75,80	76,40
9	8	80,43	82,30	82,88
10	9	85,00	87,5	87,80
11	10	88,33	90,01	90,48

samples.

Electron microscopy was performed on a Leica DM500 instrument, Germany. The device allows you to study the microstructures of solids, their local compositions and microfields (electric, magnetic, etc.) using electron microscopes (EM) - devices in which an electron beam is used to obtain enlarged images [17].

Plasma Atomic Emission Spectrometer ICPE -9000. Inductively coupled plasma atomic emission spectrometry (ICP AES) is an atomic emission spectrometry method that uses inductively coupled plasma (ICP) as a source of excitation of atoms. Inductively coupled plasma is a highly ionized inert gas (usually argon) with the same number of electrons and ions supported by a radio frequency (RF) field. The high temperature reached in the plasma sequentially desolvates, converts to vapor, excites (detection by atomic emission spectrometry (AES)) and ionizes (detection by mass spectrometry (MS)) the atoms of the test sample. Detection limits typically range from less than a nanogram (MS-ICP) to less than a microgram (AES-ICP) per liter [18].

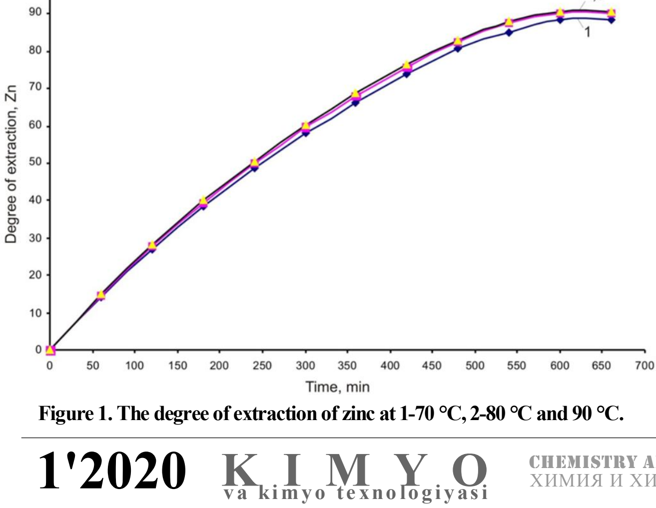

Figure 1. The degree of extraction of zinc at 1-70 °C, 2-80 °C and 90 °C.

Results and discussion

For the scientific justification of the process of producing zinc chloride from zinc concentrate of the Khandiza deposit, kinetic data are needed. For this, the effect of temperature and duration of the process of autoclave zinc extraction in a 28% hydrochloric acid solution was studied at a ratio of Zn: HCI = 1:1.1. Variable parameters were the temperature of 70, 80 and 90°C and the duration of the leaching process of 6, 8 and 10 hours. The autoclave is equipped with a thermometer, a monometer and a mechanical stirrer and has a working volume of 200 ml. The degree of zinc extraction into the solution was determined by the zinc content in the liquid phase according to the formula

$$K_{ext.} = \frac{C_o - C_\tau}{C_o} \cdot 100$$

where C_o - is the amount of zinc in the sample of zinc concentrate, C_τ- is the amount of zinc transferred to the liquid phase over time τ.

The results are shown in table 1 and Fig. 1.

It can be seen from the table and figure that an increase in the temperature of the zinc extraction process in the hydrochloric acid solution does not significantly affect the degree of extraction. So, with process duration of 6 hours at a temperature of 70°C, the degree of zinc extraction into the solution is 66.23%, at a temperature of 80 °C 68.20% and at a temperature of 90 °C 68.78%. This indicates that a temperature increase above 80 °C is not desirable.

More significantly on the degree of extraction of zinc in a hydrochloric acid solution is the duration of the process. An increase in the duration of the leaching process from 6 hours to 8 and 10 hours at a temperature of 70 °C, the degree of extraction increases from 66.23% to 80.43% and to 88.33%, respectively. At a temperature of 80 °C, these indicators are 68.20%, 82.30% and 90.01%, at a temperature of 90 °C, respectively, 68.72%, 82.88% and 90.48%.

Based on the data obtained, the reaction rates and activation energies of the process of extracting zinc from zinc concentrate with hydrochloric acid were calculated. Table 2 shows the effect of temperature and the duration of the process on the rate constant of the reaction of the interaction of zinc from the concentrate with hydrochloric acid.

It follows from the table that, with increasing temperature, the reaction rate constant for the interaction of zinc concentrate with hydrochloric acid also increases.

This is especially evident in the kinetic region, where the temperature of 343 and 353 K plays a dominant role, and then in the diffusion region with 363 K and more. Temperature practically does not affect the reaction rate constant.

Figures 2 and 3 show the changes $\lg \frac{1}{1-K_{ext.}}$ *and* $\lg K$ on the duration of the zinc leaching

Table 2

The effect of temperature and duration of the process on the reaction rate constant of the interaction of zinc with hydrochloric acid

Temperature, K	Time (τ), min	Speed constant , $K \cdot 10^{-2}$, τ^{-1}	lgK	$\ln 1/(1-K_{ext.})$
1	2	3	4	5
343	360	0,003016	-2,52057	1,52057
	480	0,003581	-2,46866	1,29159
	600	0,003953	2,44599	1,06707
	Average	**0,003217**	**-2,47841**	**1,29573**
353	360	0,003183	-2,50716	1,50243
	480	0,003608	-2,45273	1,24797
	600	0,003838	-2,425891	1,00000
	Average	**0,003543**	**-2,461927**	**1,25013**
363	360	0,003234	-2,49026	1,49443
	480	0,003678	-2,43439	1,23350
	600	0,003920	2,40671	0,97864
	Average	**0,003611**	**-2,44379**	**1,23552**

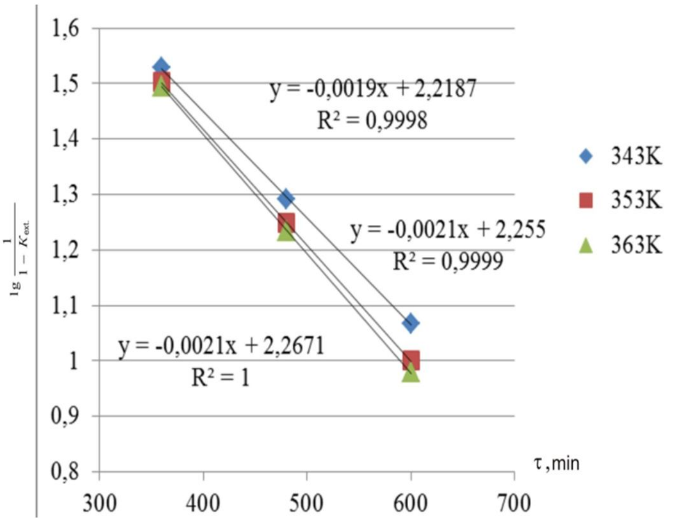

Figure 2. Dependence of ln (1/1-$K_{ext.}$) on process time and temperature.

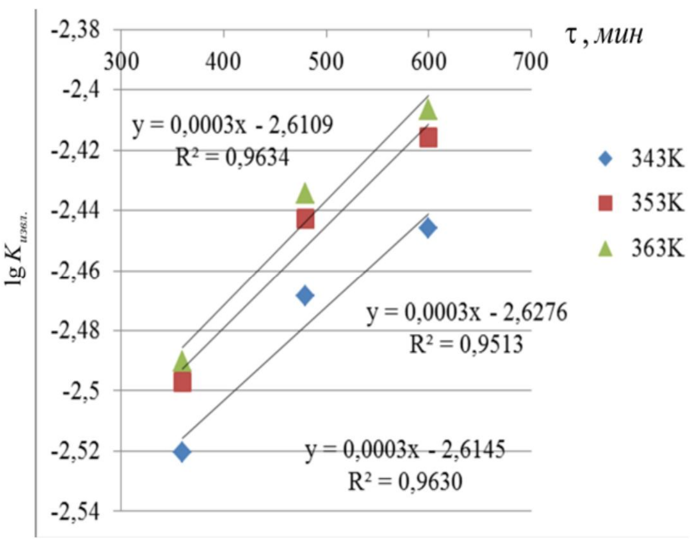

Figure 3. Dependence lg K on process time and temperature.

process. Straightforward relationship ln(1/1-$K_{ext.}$) from τ indicates the process of extracting zinc from zinc concentrate in the first order, as evidenced by correlation coefficients (R^2).

The reaction order of the zinc extraction process was determined using the first order kinetic equation [19]:

$$K = 2,303/\tau \cdot \lg C/(C_0 - C_\tau)$$

where K is the decomposition (extraction) rate constant. In our case, the formula can be represented as:

$$K = 2,303/\tau \cdot \ln(1/(1-K_{ext}))$$

The reaction rate constant for the extraction of zinc from the concentrate obeys the Arrhenius equation and is expressed by the following empirical equation [20]:

$$K = 3,08546e^{-5} \cdot \exp(4134,64/T)$$

or

$$K = 3,08546e^{-\frac{4134,64}{T}}$$

Figure 3 shows the dependence of the reaction rate constants on temperature, which is expressed by a straight line and decreases with increasing values $1/T \cdot 10^3$.

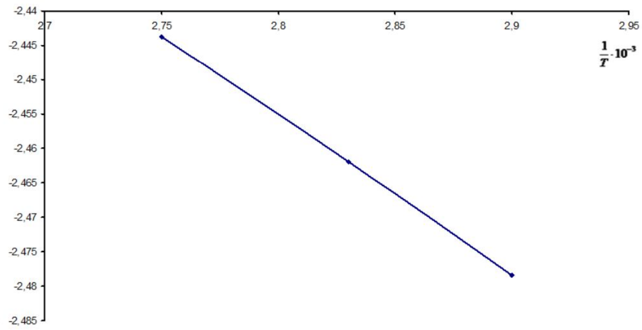

Figure 3. The dependence of the rate constant on temperature.

Table 3

The activation energy of the reaction of the interaction of zinc concentrates with hydrochloric acid

T, K	1/T·10-3	Activation energy		Average activation energy	
		E_a, kcal / mol	E_a, kJ / mol	$E_{a.mid.}$, kcal / mol	$E_{a.mid.}$, kJ / mol
2	4	6	7	8	9
343	2,9	1,45	6,09	0,97	4,05
353	2,8				
353	2,8	0,48	2,01		
363	2,7				

The established values of the reaction rate constant were the extraction of zinc from the concentrate was used to determine the apparent activation energy (E_a) (table. 3).

The average value of the process E_a is calculated by the formula [21]:

$$E_a = b \cdot 4,576$$

Depending on the temperature in the range of 343-363 K, the value of the apparent activation energy E_a of the zinc concentrate is 0.48 and 1.45 kcal/mol or 2.01 and 6.09 kJ/mol, and the average value of $E_{a\ mid.}$ is 0.97 kcal/mol or 4.05 kJ/mol, respectively.

Activation energy indices indicate sufficient reactivity of the zinc concentrate. These values can serve to assess the manufacturability of raw materials in chemical enterprises producing zinc salts.

Conclusions

Thus, the calculated data of kinetic laws confirm the reactivity of the zinc concentrate upon its decomposition with hydrochloric acid.

Its activation energy increases with temperature at a pressure of 17 atm. and the ratio of Zn:HCl = 1:1.1, and the constant of the reaction rate of the concentrate increases with increasing temperature and interaction time.

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