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METALLURGY OF NONFERROUS METALS

Study on Pure Mercurous Chloride Leaching with Sodium Thiosulfate[1]

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Abstract– Mercurous chloride (Hg_2Cl_2), also known as Calomel, is a typical mercury-containing mineral found in nature. In this work, the leaching behaviour of pure mercurous chloride dissolved in pure water and in thiosulfate solution was investigated. The mercurous chloride hardly dissolved in sulfuric acid solution at pH of 3 and pure water at pH of 6.4, with the corresponding maximum Hg extraction percentage at 3.1 and 7.5% respectively. However, the Hg extraction percentage increased to 45.8% in sodium hydroxide solution at pH of 11.2. The mercury extraction percentage reached a high of 62.6% in thiosulfate solution, and the leaching kinetics results show that the activation energy is 6.6 kJ/mol. This study indicates that the thiosulfate solution can efficiently extract mercury from mercurous chloride.

Keywords: mercurous chloride, leaching, thiosulfate, disproportionate reactions

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1. INTRODUCTION

Environmental pollution is a growing problem affecting all aspects of life. Mercury is one of the most toxic pollutants widespread in the environment [1] with the ability to be transferred through complex physical, chemical and biological transformations. For example, the atmospheric transport of Hg^0, the subsequent deposition of mercury in water and on land, and the methylation of Hg^{2+} by reducing bacteria in anoxic habitats, as well as accumulation in fish and humans through the food chain are common transformation paths [2, 3]. Mercury with high mobility and bioaccumulation can cause immense harm to human health, including pulmonary diseases in cases of acute intoxication and neurological or renal diseases from chronic poisoning [4]. More than two thousand people were affected, and 1043 people have died due to Minamata disease caused by mercury pollution from a local chemical plant in Japan in the late 1970s [5]. 5207 metric tons of mercury are released into the environment on an annual basis from natural sources, including re-emission of previously deposited mercury from both anthropogenic and natural sources [6]. In particular, soil mercury contamination has been identified at many active and previously active industrial places, such as mining sites and chemical manufacturing facilities [7–10]. Rieuwerts and Farago [11] reported that the mercury concentration in soil samples collected from the lead smelting town of Pribram (Czech Republic) was between 0.07 to 2.32 mg kg^{-1}. Stafilov et al. [12] reported a range of 0.01 to 12 mg kg^{-1} mercury in soil samples collected at the lead and zinc industrial region in the Republic of Macedonia. Bernaus et al. [13] reported that the level of mercury contamination of the soil around the chlor-alkali plant in the Netherlands reached as high as 1150 mg kg^{-1}.

As a developing country, China is different from developed countries. With rapid economic development and relatively backward technology, the production, use and emission of mercury in China are at the forefront of the World. China has paid great attention to the prevention and control of mercury pollution in recent years, and has taken different measures to control the production, processing, utilization, trade and emission of mercury, which have curbed the disordered use and discharge of mercury to some extent. Since 1994, mercury and its compounds have been included in the catalogue of toxic chemicals strictly restricted for import and export in China. Since 2002, the Ministry of Environmental Protection has carried out policy control over the import of mercury. According to the 2005 edition of the Industrial Struc-

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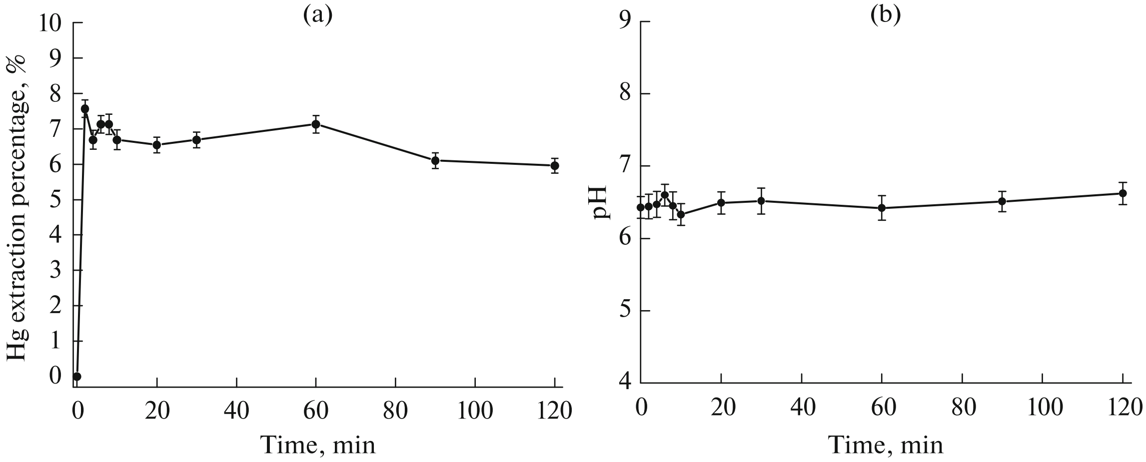

Fig. 1. The leaching of mercurous chloride in pure water: (a) Mercury extraction percentage vs. leaching time; (b) Variation in pH of mercurous chloride in pure water with time (298 K, 0.1 g Hg_2Cl_2, 500 mL pure water).

ture Adjustment Catalogue, China has eliminated some of the lagging mercury technologies and products. On April 28, 2016, the twelfth session of the standing committee of the National People's Congress (NPC) of People's Republic of China decided to approve the Minamata Convention on mercury.

For solid mercury-contaminated wastes, leaching technologies, such as soil washing using both physical and chemical separation methods to reduce contaminants concentration in wastes, have been widely used [14]. These processes can be used independently or in conjunction with other treatment methods. Chemicals such as HCl, HNO_3 and H_2O_2 have been used as lixiviants for the remediation of mercury-contaminated sediments [15]. Thiosulfate salts have also been suggested as leaching reagents for the extraction of mercury from mercury-containing soil [16]. Issaro, Besancon and Bermond [17] reported that 50 ± 5% of mercury can be extracted from the contaminated soil after leaching with 0.01 mol/L $Na_2S_2O_3$ for about 24 h. Detailed information about the leaching behaviour and mechanisms of mercuric oxide and mercuric sulfide in thiosulfate leaching systems had been investigated, indicating that the mercury extraction percentage can reach 95 and 92.37% respectively [18, 19]. As one of the typical inorganic mercury compounds found in nature, mercurous chloride was chosen for research in this paper. The leaching behaviour of Hg_2Cl_2 in thiosulfate solutions under different experimental conditions was examined and the potential use of sodium thiosulfate for the remediation of mercury-contaminated wastes is discussed.

2. EXPERIMENTAL

Reagent grade mercurous chloride and sodium thiosulfate were used as received from the local suppliers. De-ionized water with typical resistivity of 18.24 MΩ was used in all experiments. Leaching tests were carried out in a sealed beaker and mixing was performed by a magnetic agitator. Temperature was controlled through a water bath (DF-101S, Gongyi Yuhua Instrument, China). The pH of the solutions was adjusted by the addition of dilute H_2SO_4 or NaOH solutions. The solution pH was measured by a pH meter with a glass pH probe during leaching. For each test, 0.1 g mercurous chloride was leached into 500 mL of solution and a 20 mL aliquot of the slurry was taken out for sampling. The mercury concentration was measured by the atomic absorption spectrometer (AAS, INESA 4530F) in order to calculate the mercury extraction percentage.

3. RESULTS AND DISCUSSION

3.1. Water Leaching of Hg_2Cl_2

3.1.1. Pure water leaching. In order to study the water leaching of Hg_2Cl_2, a dissolution test of Hg_2Cl_2 in pure water (pH 6.4) was carried out. Variations of solution pH and mercury extraction percentage with time are shown in Fig. 1. The dissolution rate was fast, and the mercury extraction percentage reached 7.5% within 2 min. The solution pH reached a stable level of around 6.5. The solubility of Hg_2Cl_2 in pure water is calculated to 16.5 g/L (298K) based on the Fig. 1a. The Hg_2Cl_2 has higher solubility in pure water than HgS (CAS:1344-48-5, Solubility at 298 K: 0.00001 g/L) and HgO (CAS:21908-53-2, Solubility at 298 K: 0.025 g/L), but lower than $HgCl_2$ (CAS:7487-94-7, Solubility at 298 K: 74 g/L).

3.1.2. Acidic and basic water leaching. The acidic and basic leaching tests of Hg_2Cl_2 from sulfuric and sodium hydroxide solutions (pH 3 and 11.2, respectively) were carried out. Variations in solution pH and mercury extraction percentage vs. time are shown in

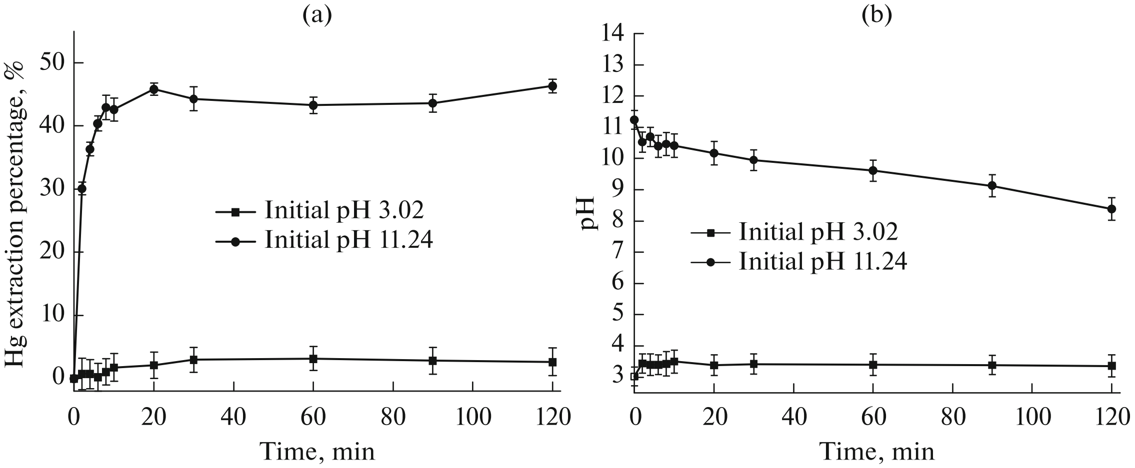

Fig. 2. The effect of pH on leaching mercurous chloride in water: (a) Mercury extraction percentage vs. leaching time; (b) Variation in pH of mercurous chloride in acidic and basic water (298 K, 0.1 g Hg_2Cl_2, 500 mL water/H_2SO_4; 500 mL water/NaOH).

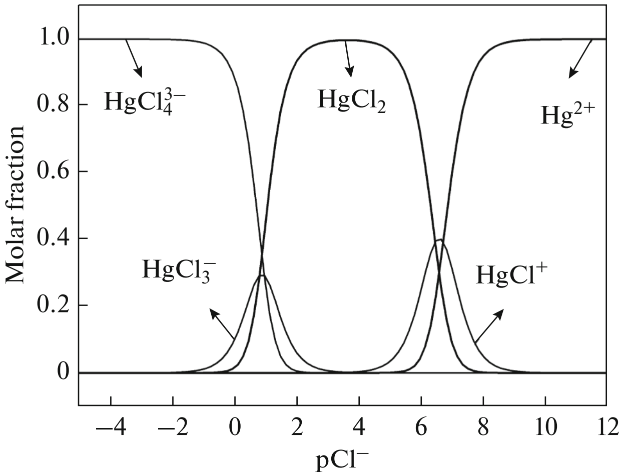

Fig. 3. Speciation diagram of the Hg–Cl–H_2O system (298 K, $[Hg]_T = 10^{-3}$ mol/L, $[Cl]_T = 0.1$ mol/L).

Fig. 2. The mercury is hardly extracted from the sulfuric solution (pH 3), reaching only 2.6%. The solution pH is fixed at 3 and remains constant. The mercury extraction percentage in basic water (pH 11.2) reached 46.3% after 120 min, much higher than in both pure and acidic water. The solution pH decreased with time, and the final pH was 8.3 after 120 min.

Mercury(II) ions react with chloride ions to form a mercury chloride complex. The coordination number can be 1, 2, 3, or 4, mainly depending on the chloride concentration. The speciation diagram of mercury chloride complex is shown in Fig. 3, based on the thermodynamic data. Increasing chloride concentration favor a higher coordination number.

The disproportionation reactions of Hg_2Cl_2 that occur during water leaching may result in the products of elemental mercury and mercury(II) ions. Different mercuric compounds exist in the solution at different pH values. The mercury species at different pH values are summarized in Table 1. The oxidation state diagram of mercury is shown in Fig. 4. As seen in Fig. 4a, when the solution pH is 0, the oxidation product of mercurous chloride is a mercuric chloride complex. The standard free energy of mercurous chloride is between that of elemental mercury and the mercuric chloride complex, and lower than the average of standard free energy of elemental mercury and the mercuric chloride complex ($k_1 < k_2$). This means that the disproportionation reaction is thermodynamically unfavorable. This could explain why mercury could be hardly extracted at a pH value of 3.0 (Fig. 2a). When the solution pH is 14 (Fig. 4b), the oxidation product of mercurous chloride is mercuric oxide. The standard free energy of mercurous chloride is between that of elemental mercury and mercuric oxide, and higher

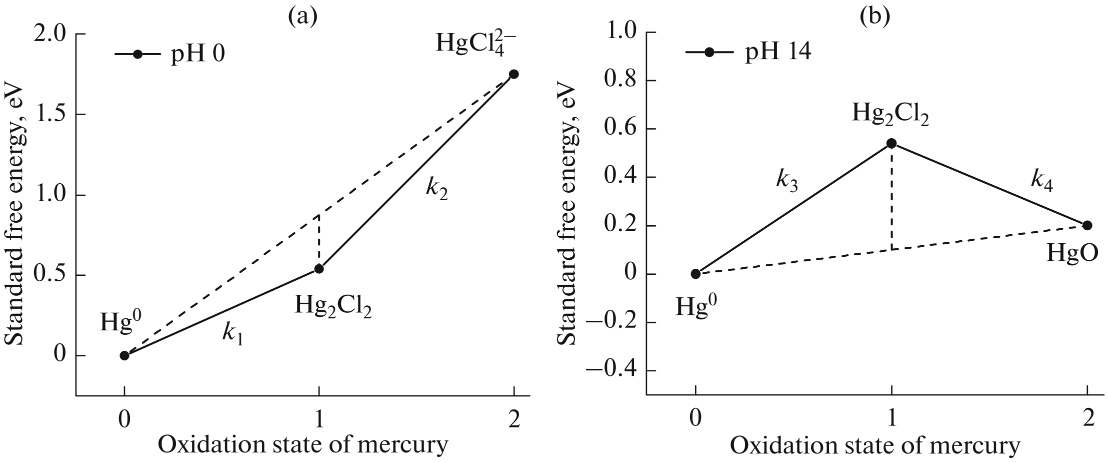

Fig. 4. The oxidation state diagram of Hg–Cl–H_2O system (298 K; (a) pH 0, (b) pH 14).

than the average of standard free energy of elemental mercury and mercuric oxide ($k_3 > k_4$). This means that the disproportionation reaction is thermodynamically favorable (equation 1). At the same time, the mercuric oxide can also be dissolved in sodium hydroxide to form mercuric hydroxide complex. This explains why mercury could be extracted at a pH of 11.2 (Fig. 2b), and the equation had been listed below.

$$Hg_2Cl_2 + 2OH^- = Hg^0 + HgO + 2Cl^- + H_2O \quad \Delta_r G_m^\Theta = -32.83 \text{ kJ/mol}. \tag{1}$$

3.2. Thiosulfate Leaching of Hg_2Cl_2

3.2.1. Effect of initial pH. The effect of initial pH on the mercurous chloride extraction with thiosulfate was studied. According to the solubility of mercurous chloride in different pH solutions, the initial pH of the solution was chosen to be 8.0, 9.9 and 10.9. The leaching results are shown in Fig. 5, where the Hg extraction percentage reached the maximum within 8 min under each unique initial pH. When pH was 8.0, the maximum Hg extraction percentage reached 57.1%. When the pH was increased to 9.9, the maximum Hg extraction percentage decreased to 47.9%. Compared with the solubility of mercurous chloride in water, it is clear that mercurous chloride leaching with sodium thiosulfate can improve the leaching rate of mercury chloride in weakly alkaline systems. As seen in Fig. 5, the solution pH gradually decreases with leaching time. It is known that higher Hg extraction percentage decreases solution pH values. According to the oxidation state diagram at high pH, the disproportionation reaction can happen spontaneously, and the mercuric ions can consume hydroxyl ions in aqueous solution, gradually decreasing the solution pH value.

3.2.2. Effect of thiosulfate concentration. The influence of thiosulfate concentration on Hg extraction percentage was studied. The concentration of sodium thiosulfate was chosen to be 0.01, 0.05, and 0.10 mol/L. The results are shown in Fig. 6. When the thiosulfate concentration was 0.01 mol/L, the maximum Hg extraction percentage was 50.5%. When thiosulfate concentration was increased to 0.05 mol/L, the maximum Hg extraction percentage reached 62.3%. However, when the concentration of thiosulfate was

Table 1. The standard free energy of mercury species in the Hg–Cl–H_2O system at different pH values (298 K, Ionic strength = 1)

pH	State	Speices	ΔG_m, eV	Equilibrium equations
pH 0	0	Hg^0	0	None
	1	Hg_2Cl_2	0.54	$Hg_2Cl_2 + 2e + 2H^+ = 2Hg^0 + 2HCl$
	2	$HgCl_4^{2-}$	1.75	$HgCl_4^{2-} + 4H^+ + 2e = Hg^0 + 4HCl$
pH 14	0	Hg^0	0	None
	1	Hg_2Cl_2	0.54	$Hg_2Cl_2 + 2e = Hg^0 + 2Cl^-$
	2	HgO	0.2	$HgO + 2e + H_2O = Hg^0 + 2OH^-$

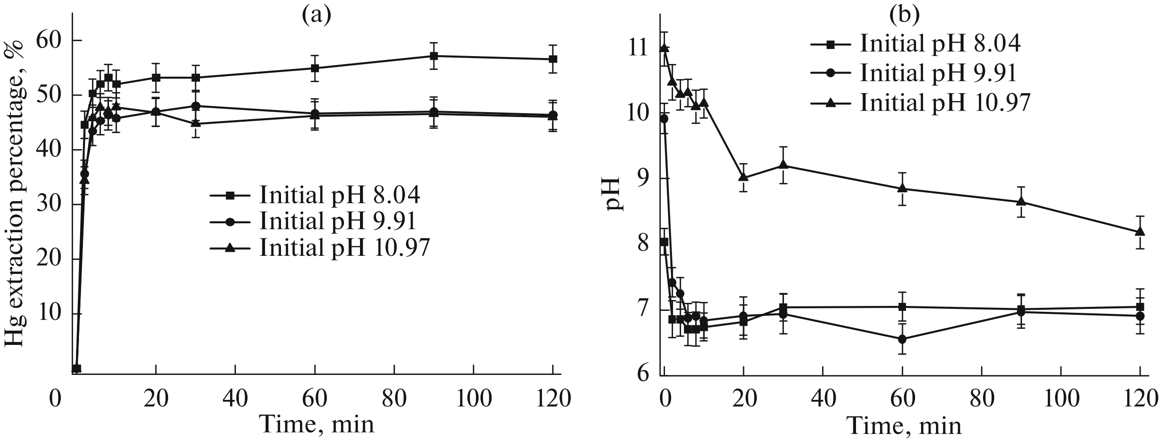

Fig. 5. (a) Hg extraction percentage and (b) pH on mercurous chloride leaching with $Na_2S_2O_3$ solution (298 K, 0.1 g Hg_2Cl_2, 0.01 mol/L $Na_2S_2O_3$ 500 mL).

increased to 0.1 mol/L, the Hg extraction percentage did not change significantly.

3.2.3. Effect of temperature. The effect of solution temperature on Hg extraction percentage was studied. The solution temperature was set at 298, 313, and 328 K. The results are shown in Fig. 7.

When the solution temperature is 298 K, the leaching rate is fast for the first 20 min and remains constant after 20 min. The Hg extraction percentage is 50.5% after 2 h. When the temperature was increased to 313 K, the leaching rate was considerably faster than at 298 K, reaching the maximum Hg extraction percentage of 60.5% at the conditions of the solid–liquid ratio of 0.1 g : 500 mL, the initial pH of 8, the $Na_2S_2O_3$ concentration of 0.01 mol/L, and the leaching time of 2 h. This is much faster, suggesting that an increase in temperature improved the solution's overall ability to leach mercury. When the temperature was increased to 328 K, the initial leaching rate of mercury was faster than at 298 and at 313 K, but remained constant after 5 min. Hg extraction percentage reached a maximum of 40.7%. Temperature increase past 313 K does not improve Hg extraction percentage from mercury chloride.

Although higher temperature initially accelerated the reaction rate, it decomposed the sodium thiosulfate, preventing further Hg extraction percentage. In the experiment, the reaction rate at 4 min was the fastest. Thus, this stage of the reaction was chosen to study the leaching kinetics based on the chemical reaction Eq. (2). The reaction rate, k_T, was calculated at different temperatures using Eq. (3). Based on the Arrhe-

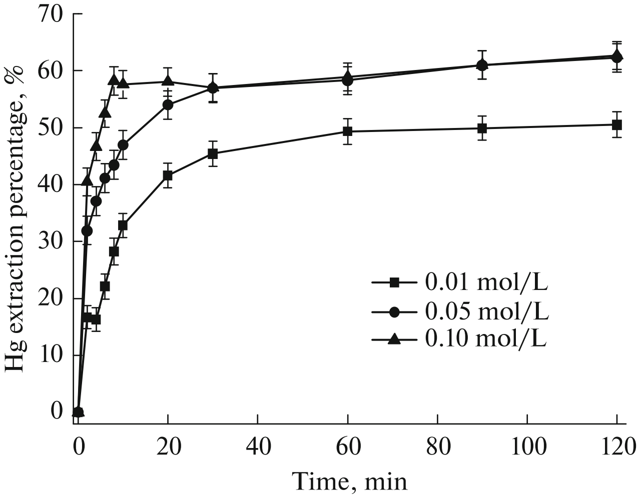

Fig. 6. Effect of thiosulfate concentration on mercurous chloride leaching with $Na_2S_2O_3$ solution (298 K, pH 8, 0.1 g Hg_2Cl_2, $Na_2S_2O_3$ 500 mL).

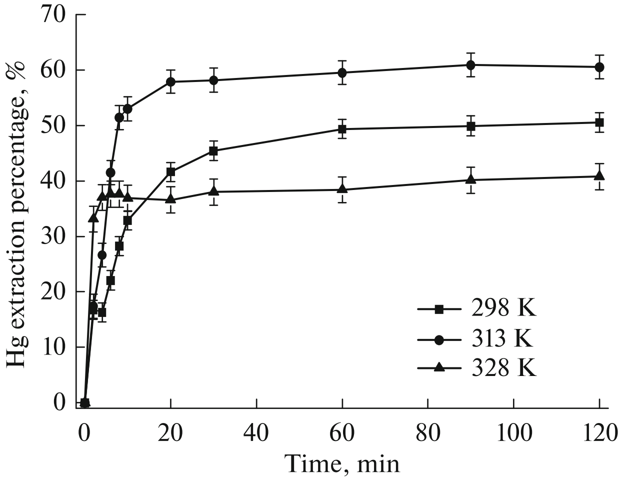

Fig. 7. Effect of temperature on mercurous chloride leaching with $Na_2S_2O_3$ solution (pH 8, 0.1 g Hg_2Cl_2, 0.01 mol/L $Na_2S_2O_3$ 500 mL).

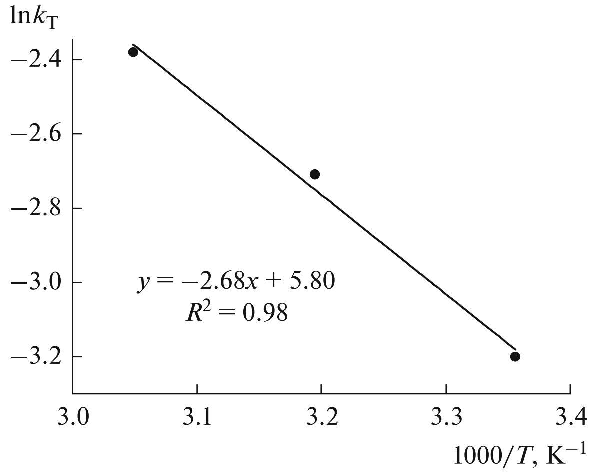

Fig. 8. Arrhenius plot of $\ln k_T$ vs. 1000/T (0.1 g Hg_2Cl_2, 0.01 mol/L $Na_2S_2O_3$ 500 mL).

nius Eq. (4), the relationship between the activation energy and the reaction rate can be fitted, as shown in Fig. 8. The fitted least-squares regression line has an R^2 value of 0.98, suggesting a good linear fit. The slope of the fitted line is negative. The final activation energy calculated from Eq. (5) is 6.6 kJ/mol.

$$\begin{aligned} &Hg_2Cl_2 + 2Na_2S_2O_3 \\ &= Hg^0 + Na_2[Hg(S_2O_3)_2] + 2NaCl, \end{aligned} \tag{2}$$

$$k_T = \frac{dX_{HgO}}{dt} = -\frac{d\dfrac{C_{Hg}}{C_{Hg}^{max}}}{dt} \approx \frac{\Delta\dfrac{C_{Hg}}{C_{Hg}^{max}}}{\Delta t}, \tag{3}$$

$$k_T = A\exp\left(-\frac{E_a}{RT}\right), \tag{4}$$

$$\ln k_T = -\frac{E_a}{RT} + \ln A. \tag{5}$$

4. CONCLUSIONS

To study the leaching mechanism, the oxidation state diagram of Hg–Cl–H_2O at different pH values was examined. Disproportionation occurs under weakly alkaline conditions. Some mercurous ions can be oxidized to mercuric oxide, which can form mercuric hydroxide complex at higher pH, and mercuric thiosulfate complex. Other mercurous ions are reduced to form elemental mercury. The leaching behaviour of pure mercurous chloride compound in water was investigated. Under pure water or acidic conditions, the Hg extraction percentage is less than 10%. However, under alkaline conditions, mercurous chloride can disproportionate and increase the Hg extraction percentage to 45.8%. The leaching behaviour of pure mercurous chloride compound with thiosulfate was investigated. The initial pH had little effect on thiosulfate leaching, while higher leaching reagent concentration increased the Hg extraction percentage. Hg extraction percentage initially decreased with temperature and then increased. When the solid-liquid ratio is 0.1 g : 500 mL, the initial pH is 8, the $Na_2S_2O_3$ concentration is 0.01 mol/L, and the leaching time is 2 h, the Hg extraction percentage can reach 60.5%. The kinetic study shows that the apparent activation energy of leaching is 6.6 kJ/mol.

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