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Kinetic regularities of hydrometallurgical recycling of spent displays: behavior of indium

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Abstract: This article discusses the physicochemical regularities of indium leaching from the surface of glass plates of used displays in various acids. The glass of used displays was pre-cleaned from polarizers and crushed. Their base is comprised of silicon and aluminum oxides. Indium is presented in the form of $In_2O_3 \cdot SnO_2$. Indium content in the material obtained is 174.8 mg/kg. Individual solutions of sulfuric, hydrochloric and methanesulfonic acids were used as leaching agents. The influence of concentrations of the mentioned acids (0.1–1.0 N), leaching duration (10–60 min), temperature (298–353 K) and liquid-to-solid ratio (L : S = (7.5÷15.0): 1 cm^3/g) on the degree of indium extraction into solution has been determined. Partial orders of reaction in terms of CH_3SO_3H, H_2SO_4, HCl are 0.69, 0.67 and 1.10, respectively. In the course of experiments an intensive increase in indium concentration was observed in the first 20–40 min f leaching in H_2SO_4 and HCl solutions. The process rate then decreased and indium extraction actually did not increase, due to a fall in the amount of non-reacted indium. During leaching in 0.1–0.4 N in CH_3SO_3H solutions, the rate of indium dissolution did not change throughout the experiment, since the amount of non-reacted indium gas decreased insignificantly. The acids considered here can be ranked in the following ascending order of their efficiency for indium dissolution: CH_3SO_3H, H_2SO_4, HCl, which corresponds to the growth of strengths of these acids. An increase in the temperature led to a significant increase in indium extraction. The apparent activation energies of In_2O_3 dissolution in CH_3SO_3H, H_2SO_4, HCl solutions have were calculated as equal to 51.4, 51.2, 43.4 kJ/mole, respectively. It was established that with the use of HCl as leaching agent, the increase in the fraction of liquid phase in the slurry from 7.5 : 1 to 15 : 1 cm^3/g lead to fall in indium extraction by 2.4 times and the initial leaching rate by 3.2 times. It was demonstrated that an increase in L : S during indium dissolution in CH_3SO_3H (from 7.5 : 1 to 15 : 1 cm^3/g) and H_2SO_4 (from 10 : 1 to 15 : 1 cm^3/g) is accompanied by insignificant changes in extraction and initial leaching rate. Therefore, the studies performed demonstrated that indium leaching from glasses of spent displays flows in mixed mode upon the use of HCl and in kinetic mode in H_2SO_4 and CH_3SO_3H solutions.

Keywords: indium, leaching, hydrochloric acid, sulfuric acid, methanesulfonic acid, kinetics, apparent activation energy, order of reaction

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Кинетические закономерности гидрометаллургической переработки отслуживших дисплеев: поведение индия

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Аннотация: Изучены физико-химические закономерности выщелачивания индия с поверхности стеклянных пластин отработанных дисплеев в различных кислотах. Стекла отслуживших дисплеев были предварительно очищены от поляризаторов и

измельчены. Их основу составляли оксиды кремния и алюминия. Индий представлен в виде соединения $In_2O_3 \cdot SnO_2$. Содержание индия в полученном материале составляло 174,8 мг/кг. В качестве выщелачивающих агентов использовали индивидуальные растворы серной, соляной и метансульфоновой кислот. Установлено влияние концентраций указанных кислот (0,1–1,0 н), продолжительности выщелачивания (10–60 мин), температуры (298–353 K) и соотношения жидкого к твердому (Ж : Т = = (7,5÷15,0) : 1 $см^3$/г) на степень извлечения индия в раствор. Частные порядки реакций по CH_3SO_3H, H_2SO_4, HCl составили 0,69, 0,67 и 1,10 соответственно. В ходе экспериментов наблюдалось интенсивное повышение концентрации индия в первые 20–40 мин выщелачивания в растворах H_2SO_4 и HCl, после чего скорость процесса снижалась и извлечение индия практически не росло вследствие уменьшения количества непрореагировавшего индия. При выщелачивании в 0,1–0,4 н растворах CH_3SO_3H скорость растворения индия не менялась на всем протяжении эксперимента ввиду того, что количество непрореагировавшего индия снижалось незначительно. Исследуемые кислоты можно расположить в следующий ряд в порядке возрастания их эффективности в растворении индия: CH_3SO_3H, H_2SO_4, HCl, что соответствует росту сил данных кислот. Увеличение температуры значительно повышало извлечение индия. Рассчитаны значения кажущейся энергии активации растворения In_2O_3 в растворах CH_3SO_3H, H_2SO_4, HCl, составившие 51,4, 51,2, 43,4 кДж/моль соответственно. Обнаружено, что при использовании в качестве выщелачивающего агента HCl увеличение доли жидкой фазы в пульпе от 7,5 : 1 до 15 : 1 $см^3$/г снижало извлечение индия в 2,4 раза, а начальную скорость выщелачивания – в 3,2 раза. Показано, что повышение Ж : Т при растворении индия в CH_3SO_3H (с 7,5 : 1 до 15 : 1 $см^3$/г) и H_2SO_4 (с 10 : 1 до 15 : 1 $см^3$/г) сопровождается незначительным изменением извлечения и начальной скорости выщелачивания. Таким образом, проведенные исследования показали, что выщелачивание индия из стекол отслуживших дисплеев протекает в смешанном режиме при использовании HCl и в кинетическом режиме в растворах H_2SO_4 и CH_3SO_3H.

Ключевые слова: индий, выщелачивание, соляная кислота, серная кислота, метансульфоновая кислота, кинетика, кажущаяся энергия активации, порядок реакции

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Introduction

In the recent 20 years the structure of indium consumption has significantly changed. This metal was previously mainly used for fabrication of alloys, electrical components, and semiconductors. At the present time, the major portion of indium is used in the form of indium-tin oxide (ITO). The latter is the solid solution of indium and tin oxides (90 % In_2O_3, 10 % SnO_2) characterized by semiconductor properties and transparency in visible light. Due to these properties ITO is essential in production of LED and OLED displays, solar cells, inter alia.

The main source of indium is zinc sulfide ore, with a content of 1—100 g/t [1]. At the existing level of indium consumption (about 1500 t/year) [2], its reserves in mineral ores will be sufficient only for the next decade. Used monitors are the most promising secondary source of indium.

In Russia the reprocessing of used displays is limited to the disposal of boards and luminescent lamps. At present displays are recycled only in a few countries (South Korea, Japan, and Belgium) due to the low content of valuable metals and complex composition of products.

Displays include several layers: polarizers, glass plates, liquid crystals. The glass plates are coated with ITO layer with a thickness of 50—200 nm. The indium content in them is 100—350 mg/kg [2, 3]. On the reverse side of glass substrate a polarizer layer from polyvinyl acetate film is applied.

Preliminary preparation of glass plates before reprocessing can include the stages of crushing and grinding [4]. However, the presence of polarizer film makes disintegration more difficult. High temperature processing at T = 453÷493 K allows the polarizer to be embrittled, thus increasing the efficiency of glass crushing [4, 5]. Moreover, it is possible to separate ITO particles from glass substrate by thermal processing at T = 923 K in 8—10 min and subsequently removing the product by compressed air [6]. Other methods of ITO concentrating include gravimetric separation [4], floatation [7], abrasive processing of glass surface [8, 9] and others.

Pyrometric techniques allow oxides of indium and tin to be recovered [10, 11] and then distilled, including in the form of chlorides [12]. Hydrometallurgical reprocessing procedures of glass plates include leaching in various acids (sulfuric [8, 9, 13, 14], hydrochloric [15], nitric [16], citric, malic [17]) with subsequent concentrating and separation of metals by liquid extraction [15, 18, 19] (di-(2-ethylhexyl) phosphoric acid, tributyl phos-

phate) and sorption [20, 21] (Lewatit TP 208, Lewatit VP OC 1026). The dissolution processes can be intensified by oxidizing and reducing agents [22], as well as by ultrasound processing [6, 23, 24], and so on.

This work presents a comparative assessment of the kinetics of indium leaching from the surface of glass plates of spent displays in sulfuric, hydrochloric and methanesulfonic acids. The latter is considered as "green" organic acid due to its relatively low toxicity, biodegradability, high boiling point and very low pressure of saturated vapors [25, 26]. In addition, methanesulfonic acid is characterized by high electrical conductivity, and its salts are highly soluble in water [25]. In recent years this acid has been considered as a leaching agent in studies on the reprocessing of copper, zinc, bismuth raw materials [26—28], as well as in the technology of The Paroo Station (Australia) for lead extraction from cerussite ore [29, 30].

The acids applied in this work are referred to as strong: they can be arranged in the ascending order of increase in their strength expressed in terms of the dissociation constant (pK_{a1}): CH_3SO_3H (–1,86), H_2SO_4 (–3), HCl (–7) [31, 32].

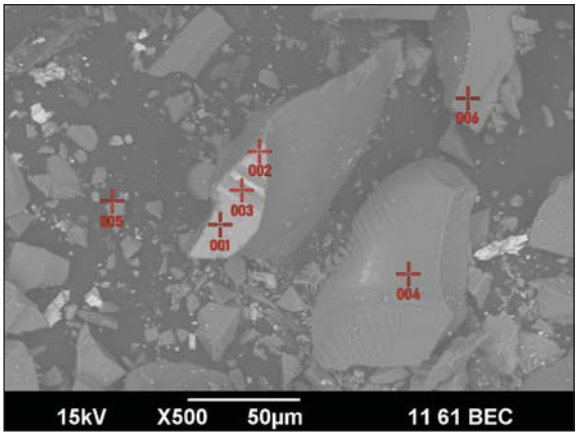
The aim of this work is to analyse the influence of the concentration of acids, duration, temperature and slurry density on physicochemical regularities of dissolution of indium from the surface of glass plates of spent displays.

Experimental

Materials, equipment and research methods

Glass from used monitors was first washed with water, dried in air, then held at 463 K for softening and manual removal of film. The cleaned glass was crushed in a rod mill. After sieving, the –1 mm fraction of crushed glass was separated for further experiments. After thorough mixing of the material, a representative sample was selected by means of quartering. This was then used for subsequent chemical analysis using a novAA 300 atomic absorption spectrophotometer (AAS) ("Analytik Jena", Germany). The particle size of the material was determined using a HELOS&RODOS laser diffraction analyzer of particle sizes ("Sympatec GmbH", Germany). The morphology of crushed glass samples and their chemical composition were analyzed using a JEOL JSM-6390LA scanning electron microscope (Japan), equipped with a JED-2300 system of energy dispersion microanalysis.

The main bulk of the material (>85 %) included particles of irregular shape with a size of less than 300 μm (Fig. 1, 2). According to the data of elemental analysis and previous studies [3, 12], the oxides of aluminum, silicon, and calcium prevailed in the material. Indium



Element	Number of measurement region					
	001	002	003	004	005	006
	Content,%					
Na	1.0	0.8				
Mg				1.7	4.0	1.3
Al	2.8	8.6	12.9	19.1	20.2	14.3
Si	69.0	74.4	77.4	68.5	69.0	56.8
Ca	4.1	4.0	3.2	10.7	6.8	27.6
Mo			6.5			
In	19.9	10.1				
Sn	3.2	2.1				

Fig. 1. SEM image and elemental composition of crushed display glass

Рис. 1. СЭМ-изображение и элементный состав измельченных стекол дисплеев

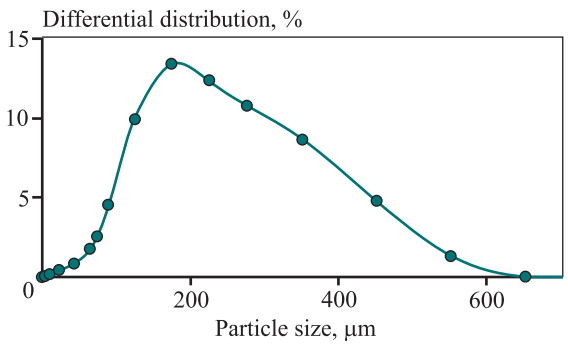


Fig. 2. Particle size distribution of crushed display glass

Рис. 2. Гранулометрический состав измельченных стекол дисплеев

and tin compounds were present on the glass surface (points *1*, *2* in Fig. 1), Molybdenum compounds were present on the surface of conducting tracks (point *3*, Fig. 1). The crushed display glass contained, mg/kg: In — 174.8, Sn — 1.7.

In the experiments, H_2SO_4 sulfuric acid (chemical pure grade), HCl acid (chemically pure grade) and CH_3SO_3H methanesulfonic acid (chemically pure grade) were used. The initial solution of the acids were prepared by distilled water dilution, and agitated using a magnetic stirrer.

Leaching of crushed glasses

The leaching experiments were carried out in a 0.5 dm^3 thermostatic reactor at T = 298÷353 K, τ = = 10÷60 min, concentration of acids 0.1—1.0 N, liquid to solid ratio L : S = (7.5÷15.0) : 1 cm^3/g. While varying L : S, the mass ratio of hydrogen and indium ions was maintained at a constant in the sample (10 mg H^+/1 mg In). Respectively, the concentrations of acids in this series of experiments varied from 0.15 to 0.3 N.

Solutions of acids with preset concentration were poured into the reactor, sealed, and heated to preset temperature with continuous stirring. Then a sample of material (20 g) was loaded into the reactor and the slurry temperature was automatically maintained with an accuracy of ±2 K.

The slurry after leaching was filtered, and the cake was washed with distilled water. Then the cake was treated at T = 363 K in 20 % solution of hydrochloric acid in several hours for complete passing of metals into solution. Then the cake was also filtered and washed with distilled water. Samples taken during leaching, filtrates after leaching and treatment with acid. The washing waters were also analyzed for content of indium ions using an AAS novAA300 ("Analytik Jena", Germany). Total indium extraction (α_{In}) was assessed by its content in the filtrates and washing waters.

Experimental data processing

The degree of indium extraction was assessed accounting for volumes of taken samples using the following equation:

$$\alpha_{In}^{i} = \frac{C^i[V_{исх} - V_{пр}(i-1)] + \sum_1^{i-1}(C^i V_{пр})}{G_{In}} \cdot 100\ \%, \quad (1)$$

where α^i_{In} is the degree of indium extraction at the time of taking the i-th sample, %; C^i is the concentration of indium in the i-th sample, g/dm^3; V_{sample} is the sample volume, dm^3; V_{ini} is the initial volume of leaching solution, dm^3; and G_{In} is the indium weight in the sample, g.

The kinetic properties (partial orders of reactions, apparent activation energy) were determined by detection of instant leaching rate at initial time (υ_0) by plotting tangents to the curves $\alpha_{In} = f(\tau)$. The tangents were plotted via the coordinate origin.

The generalizing equation for the rate of indium leaching can be written as follows:

$$\frac{d\alpha}{d\tau} = k(T, \nu)[C(\alpha)]^n [P(\alpha)]^m S(\alpha), \quad (2)$$

where k is the rate constant depending on temperature and, in the case of diffusion or mixed mode, on speed of liquid motion with regard to the surface of solid particles (ν). C and n are the concentration of acids and partial order in terms of concentration, respectively. P and m are the slurry density and partial order in terms of slurry density, respectively. $S(\alpha)$ is the function describing the cumulative surface area of reaction, as a function of extent of reaction behavior (determine by the particle shapes and particle size distribution).

Results and discussion

The influence of concentration of acids on indium extraction

The data obtained (Fig. 3) shows the changes in the pattern of dependences $\alpha_{In} = f(\tau)$ in the case of various acids. Thus, for instance, in H_2SO_4 and HCl solutions (Fig. 3, *a*, *b*) in the first 20—40 min of leaching, the intensive dissolution of indium was observed. Then the process rate significantly decreased due to a decrease in the amount of non-reacted ITO (see Fig. 3, *a*, curves *3*, *4* and Fig. 3, *b*, curves *2—4*), also in the concentration of H^+ ions (Fig. 3, *a*, curves *1*, *2* and Fig. 3, *b*, curve *1*). In the case of 0.1—0.4 N CH_3SO_3H solutions, the plots $\alpha_{In} = f(\tau)$ were a straight line. The rate of indium dissolution actually did not change throughout the experiments (Fig. 3, *c*) due to low extraction and the high amount of non-reacted indium.

At a relatively low concentration of leaching agents (0.1—0.2 N), the indium extraction in 60 min was higher in HCl solutions (α_{In} = 50÷100 %) than in solutions of H_2SO_4 (α_{In} = 43÷76 %) and CH_3SO_3H (α_{In} = 25÷39 %). With an increase in the acid concentration to 0.4—1.0 N already at 40 min, the indium is extracted nearly completely into H_2SO_4 and HCl solutions (α_{In} = 97÷100 %). On the other hand, its extraction (α_{In} = 84 %) with the

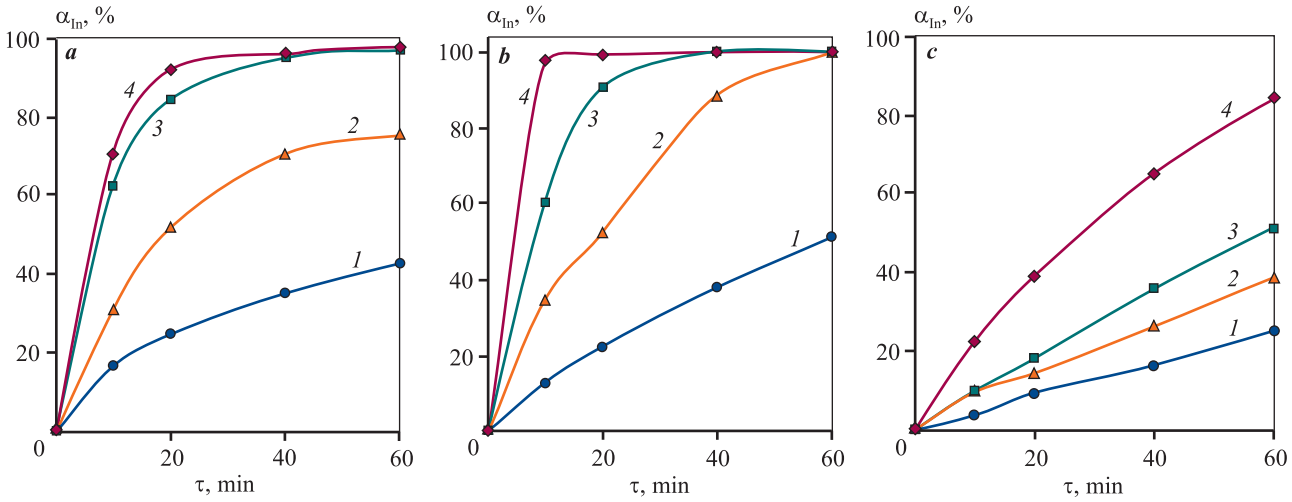


Fig. 3. Indium recovery as a function of leaching duration at different concentrations of H_2SO_4 (***a***), HCl (***b***) and CH_3SO_3H (***c***)
T = 333 K; L : S = 10 : 1 cm^3/g; C_{acids}; N: 0.1 (***1***), 0.2 (***2***), 0.4 (***3***) and 1.0 (***4***)

Рис. 3. Влияние продолжительности выщелачивания на извлечение индия при различных концентрациях H_2SO_4 (***a***), HCl (***b***) и CH_3SO_3H (***c***)
T = 333 K; Ж : Т = 10 : 1 $см^3/г$; $C_{кислот}$, н: 0,1 (***1***), 0,2 (***2***), 0,4 (***3***) и 1,0 (***4***)

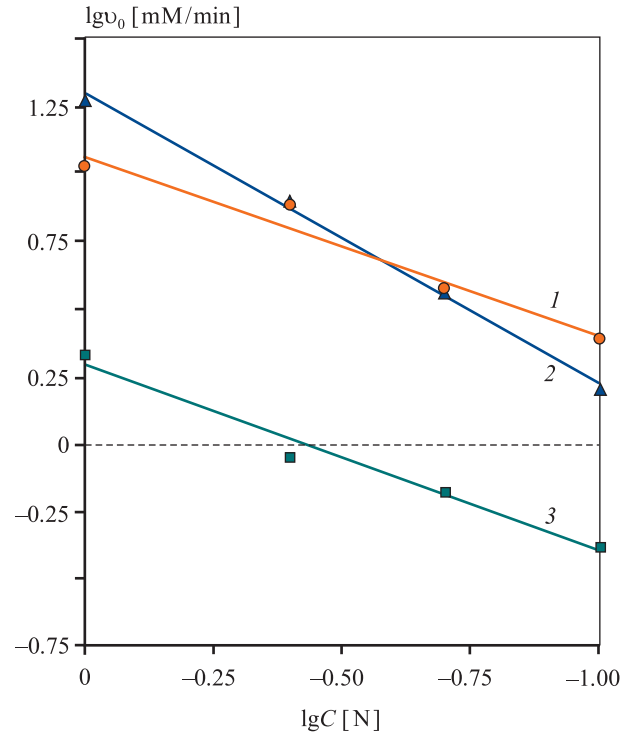


Fig. 4. Determination of partial orders of indium leaching reactions in different acids
1 – H_2SO_4, ***2*** – HCl, ***3*** – CH_3SO_3H

Рис. 4. Определение частных порядков реакций выщелачивания индия в различных кислотах
1 – H_2SO_4, ***2*** – HCl, ***3*** – CH_3SO_3H

use of CH_3SO_3H was achieved only at $C_{CH_3SO_3H}$ = 1.0 and in 60 min of leaching.

Partial orders of indium leaching in terms of H_2SO_4, HCl and CH_3SO_3H, were determined by the angle coefficients of lines plotted in lgυ$_0$—lg$C$ coordinates (Fig. 4), were 0.67, 1.10 and 0.69, respectively.

The values obtained for α_{In} and the regularities of their variation are in good agreement with the dissociation coefficients of acids. Thus, HCl was dissociated nearly completely, and its apparent extent of dissociation varies insignificantly with an increase in concentration, contrary to H_2SO_4 and CH_3SO_3H. The increase in HCl concentration leads to proportional increase in CH^+, hence to an increase in α_{In}, υ$_0$. In H_2SO_4 and CH_3SO_3H solutions, the release of free H^+ ions is restricted by interionic interactions.

The influence of temperature on indium extraction

A temperature increase from 298 to 353 K naturally leads to increased indium extraction from H_2SO_4, HCl and CH_3SO_3H solutions by 83, 87 and 67 %, respectively (Fig. 5). At low temperatures (298—313 K), the efficiency of CH_3SO_3H was minimum .At T = 298 K, the indium oxide in fact did not dissolve, and at 313 K it did not exceed 10 % (Fig. 5, *c*).

The minimum indium extraction at T = 353 K, C_{acids} = 0.2 N was obtained with the use of CH_3SO_3H (70 % in 60 min), and the maximum extraction was

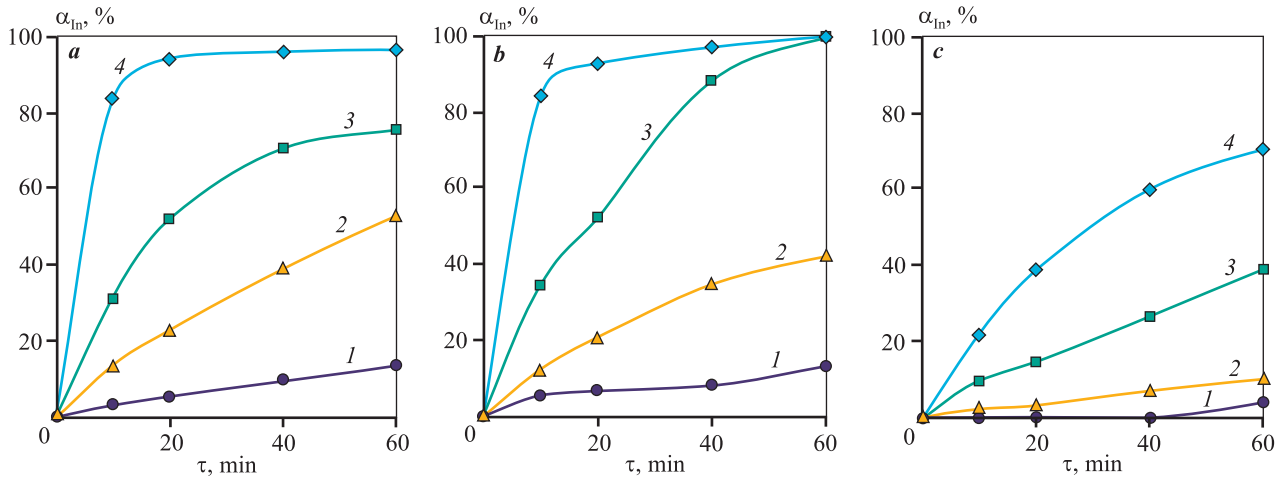


Fig. 5. Influence of leaching duration on Indium extraction as a function of leaching duration in H_2SO_4 (***a***), HCl (***b***) and CH_3SO_3H (***c***) solutions at different temperatures
L : S = 10 : 1 cm^3/g; C_{acids} = 0.2 N; *T*, K: 298 (***1***), 313 (***2***), 333 (***3***) and 353 (***4***)

Рис. 5. Влияние продолжительности выщелачивания на извлечение индия в растворах H_2SO_4 (***a***), HCl (***b***) и CH_3SO_3H (***c***) при различных температурах
Ж : Т = 10 : 1 $см^3$/г; $C_{кислот}$ = 0,2 н; *T*, K: 298 (***1***), 313 (***2***), 333 (***3***) и 353 (***4***)

in HCl solution (100 % in 60 min). During leaching in H_2SO_4 and HCl solutions at T = 353 K, the major portion of indium was dissolved in the first 10—20 min.

The kinetic regularities obtained allowed the apparent activation energy (E_a) of indium oxide dissolution in various acids to be calculated (Fig. 6): H_2SO_4 — 51.2 kJ/mole, HCl — 43.4 kJ/mole, CH_3SO_3H — 51.4 kJ/mole. The values E_a for the reactions of In_2O_3 with H_2SO_4 and CH_3SO_3H are sufficiently close and in combination with the obtained values of partial orders in terms of acids evidence process run in kinetic mode. Most probably, the leaching in these acids is limited by their dissociation with subsequent interaction of H^+ ions with ITO. Similar E_a of In dissolution in H_2SO_4 was obtained in [34]. The apparent activation energy of In dissolution in HCl solution and the partial order in terms of acid, the process runs in mixed mode.

The influence of slurry density on indium extraction

In this series of experiments the indium behavior was assessed at various slurry densities, maintaining a constant flow rate of hydrogen ions and slurry temperature. The results obtained (Fig. 7) confirm the significant influence of diffusion on indium leaching from ITO in solutions of hydrochloric acid. With an increase in the fraction of liquid phase in the slurry (from 7.5 : 1 to 15 : 1 cm^3/g) α_{In} decreased by 2.4 times, and

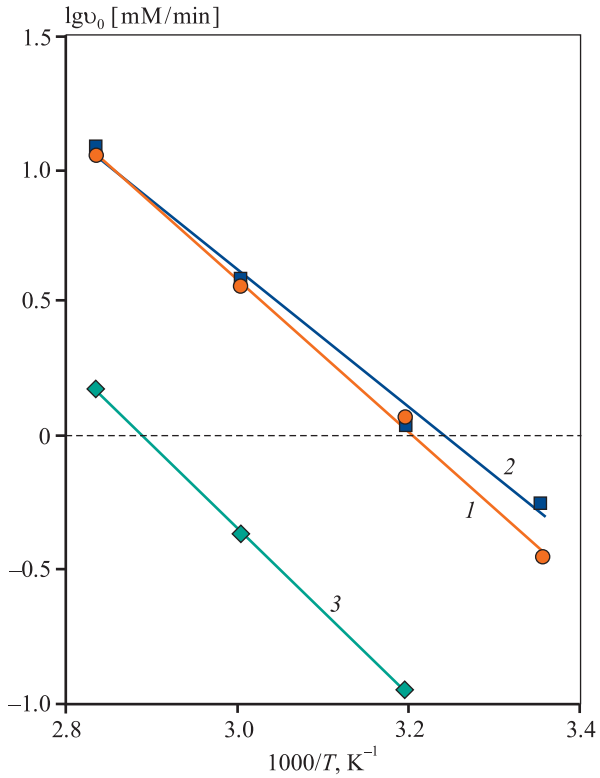


Fig. 6. lgυ$_0$ as a function of $1/T$ for determination of apparent energy activation of indium dissolution in different acids
1 – H_2SO_4, ***2*** – HCl, ***3*** – CH_3SO_3H

Рис. 6. Графики зависимости lgυ$_0$ от $1/T$ для определения кажущейся энергии активации растворения индия в различных кислотах
1 – H_2SO_4, ***2*** – HCl, ***3*** – CH_3SO_3H

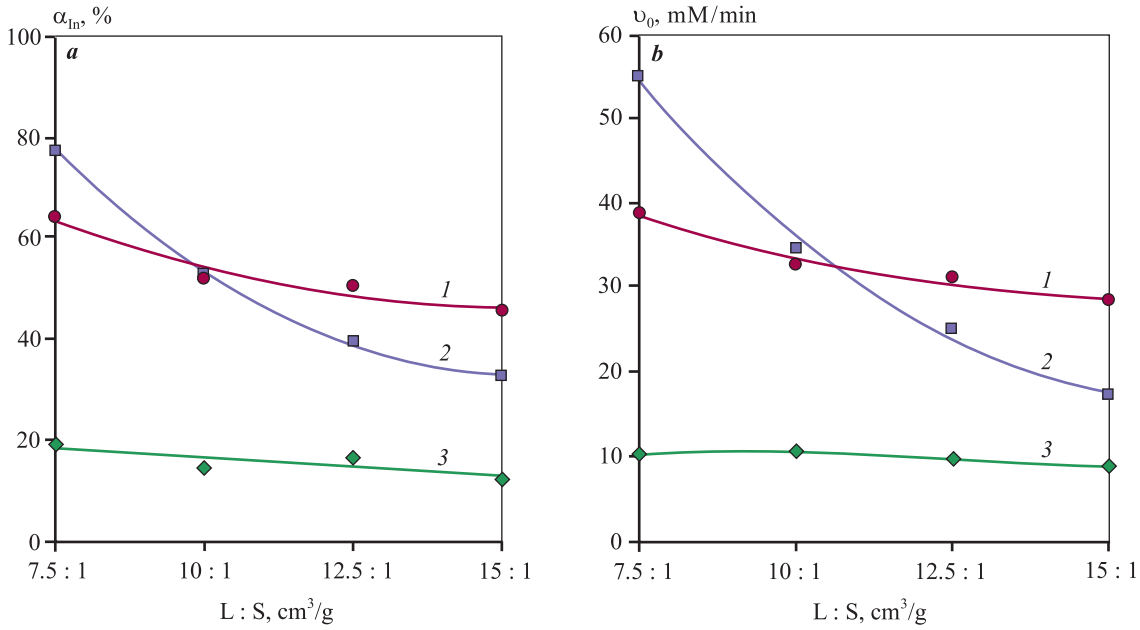


Fig. 7. Extraction (at τ = 20 min) (***a***) and initial leaching rate from solutions of different acids (***b***) as a function of slurry density

1 – H_2SO_4, ***2*** – HCl, ***3*** – CH_3SO_3H; T = 333 K

Рис. 7. Влияние плотности пульпы на извлечение (при τ = 20 мин) (***a***) и начальные скорости выщелачивания (***b***) индия из растворов различных кислот

1 – H_2SO_4, ***2*** – HCl, ***3*** – CH_3SO_3H; T = 333 K

υ_0 decreased by 3.2 times. In solutions of sulfuric acid with an increase in the fraction of liquid phase from 7.5 : 1 to 10 : 1 cm^3/g, α_{In} decreased by 12 %, and υ_0 by 6 mmol/min. Upon further increase in the volume of liquid in the slurry (L : S = (10÷15) : 1) both properties varied insignificantly. In the solutions of methanesulfonic acid in overall L : S range, α_{In} varied by 5 %, and υ_0 by 2 mmol/min.

Therefore, upon indium leaching in H_2SO_4 (L : S = = (10÷15) : 1) and CH_3SO_3H (L : S = (7.5÷15) : 1) solutions, the influence of slurry density was minimum.

Conclusions

The studies performed aimed at establishing the influence of acids (H_2SO_4, HCl and CH_3SO_3H), their concentrations (0.1—1.0 N), temperature modes (298—353 K), slurry density (L : S = (7.5÷15.0) : 1) and leaching duration (10—60 min) of used monitors demonstrated the fundamental influence of these parameters on kinetics of indium extraction into solution. The following conclusions were obtained on the basis of the obtained experimental results.

1. In the overall range of the considered acids, a high efficiency of hydrochloric acid was detected. Using this acid, 100 % indium extraction was achieved in 40 min of leaching in 0.4 N solution at T = 333 K. The increase in the HCl concentration to 1.0 N decreased the process duration to 10 min.

2. An increase in the leaching temperature allows significant improvement in indium extraction. The values of apparent activation energy of indium leaching obtained show evidence of the predominant process in kinetic mode with the use of sulfuric and methanesulfonic acids, and in mixed mode upon leaching in hydrochloric acids.

3. An increase in the fraction of liquid phase in the slurry (at constant flow rate of hydrogen ions to indium) leads to a decrease in extraction and initial rate of indium dissolution in hydrochloric acid solutions. During leaching in solutions of sulfuric and methanesulfonic acids, an insignificant influence of slurry density on extraction and initial rates of indium dissolution was observed.

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