

Yaroslav Kalymon, Andriy Helesh and Oleg Yavorskyi

HYDROLYTIC SULPHATE ACID EVAPORATION BY WASTE GASES FROM BURNING FURNACES OF META-TITANIC ACID PASTE

*Lviv Polytechnic National University
12, Bandera str., 79013 Lviv, Ukraine
an_gel@polynet.lviv.ua*

Received: June 02, 2012 / Revised: June 22, 2012 / Accepted: September 09, 2012

© Kalymon Y., Helesh A., Yavorskyi O., 2012

Abstract. The advisability of hydrolytic sulphate acid evaporation by waste gases from burning furnaces of meta-titanic acid paste has been theoretically grounded and practically proved. The optimum regime of the evaporation process has been determined and mass-transfer apparatus has been designed. The high intensity of the process has been confirmed by experiments. The dependence of the motive force and waste gases moisture on the heat transfer factor has been determined.

Keywords: hydrolytic sulphate acid, waste gases.

1. Introduction

Hydrolytic sulphate acid is obtained at pigment titanium(IV) oxide production and contains 18–25 mas % of H_2SO_4 , 5.5–6.5 mas % of FeSO_4 and other soluble salts. During the production of 1 ton of TiO_2 5–6 tons of hydrolytic sulphate acid are obtained or 1.25 tons to calculate for 100 % H_2SO_4 . Taking into account the great volumes of pigment titanium(IV) oxide production (world output was $5.4 \cdot 10^6$ tons in 2005; the Ukrainian part is 2 %), it is obvious that the great amount of hydrolytic sulphate acid is produced as well [1].

Many enterprises only partially use this acid for the production of fertilizers; the greater part is dumped to the tailing pit. The results are loss of valuable chemical product (H_2SO_4), the increase of cost price of pigment titanium(IV) oxide and considerable harm to the environment. Therefore the search of rational and economic method of hydrolytic sulphate acid utilization is very urgent.

The concentration of above-mentioned acid to the standard one (92–94 % H_2SO_4) is a complicated and unprofitable process. Therefore it is advisable to use the hydrolytic acid in the production without strict demands to the process conditions. Thus, the amophose production is

present at the production of pigment titanium(IV) oxide. Due to the production demands, the sulphate acid containing no less than 54–55 % of H_2SO_4 and no more than 1.36 % of FeSO_4 (0.5 % Fe^{2+}) may be used.

Usually natural gas is used as a heat transfer for the evaporation of sulphate acid. In connection with the constant growth of natural gas cost, this method became unprofitable. The alternative to the natural gas may be waste gases from the burning furnaces of meta-titanic acid paste.

The aim of this work is to ground theoretically and confirm in practice the advisability of hydrolytic sulphate acid evaporation by the waste gases from the burning furnaces of meta-titanic acid paste.

2. Experimental

2.1. Theoretical Part

The burning of meta-titanic acid wet paste followed by TiO_2 rutile form obtaining is one of the stages for the production of pigment titanium(IV) oxide. The process is carried out in rotating drum-type furnaces using furnace gases which are obtained by natural gas burning. The temperature of the gases at the exit is 623–673 K. The gases consist of water steam (18 vol %), H_2SO_4 mist (1.5–2.0 g/m^3), HCl (0.15–0.2 g/m^3), NO (0.1–0.2 g/m^3) and TiO_2 dust (1.5–2.0 g/m^3). The gases are washed by water at 343 K and thrown out to the atmosphere. During the washing the gases are partially purified from contaminants and TiO_2 dust, but the mentioned process does not intend the utilization of gases heat and has not the sufficient deuration degree [2].

On the basis of above-mentioned characteristics of waste gases and calculations of material and heat balances made by us the following resume may be done.

1. The concentration of water steam of waste gases from burning furnaces (dew point) passes at 334–335 K. It means that under direct contact between waste gases and hydrolysis acid the gases temperature may be reduced from 623–673 K to even 393–373 K.

2. The heat content of waste gases is 985–1090 kJ/m³ (473–459 kJ/m³ is for water steam and 526–618 kJ/m³ – for nitrogen, carbon(IV) oxide and oxygen). During the gases cooling from 623–673 K to 373 K their heat content decreases to 529 kJ/m³. It means that 456–561 kJ/m³ ([985–1090] – 529) may be used both for the heating of hydrolytic sulphate acid from the initial temperature (303–313 K) to the evaporation temperature and for the water evaporation from hydrolytic acid.

3. The calculations show that during the hydrolytic acid evaporation from 20 to 55 % H₂SO₄ at the initial temperatures of 313 K (for acid), 676 K (for waste gases) and gases end temperature of 373 K the consumption of gases heat content for the acid heating is 55 kJ/m³. Thus 506 kJ/m³ may be used for water evaporation from hydrolysis acid. Under the adiabatic conditions of evaporation process the waste gases lose their heat content slightly, because gases heat used for water evaporation transfer into waste gases together with water steam. The heat of waste gases may be utilized, for example for water heating or common necessities.

4. We calculated the temperatures to which the acid may be heated and waste gases may be cooled. Thus the temperature is 358 K for the acid end concentration of 55 %.

5. During the obtaining of 1 ton of pigment titanium(IV) oxide 14.5 thousands m³ of waste gases are thrown out to the atmosphere (or (14.3–15.8)·10⁶ kJ of heat). Under the direct contact between acid and waste gases the latter ones may be cooled to 373–393 K. The heat of cooling from 623–673 K to 373–393 K is (6.6–8.1)·10⁶ kJ. To evaporate 1 ton of 20 % H₂SO₄ to 55 % H₂SO₄ we need 1.62·10⁶ kJ. We assume the heat leakage of 10 %. Then during the production of 1 ton of pigment titanium(IV) oxide we may utilize 3.6–4.8 tons $\left(\frac{6.6-8.7}{1.62} \cdot 0.9\right)$ of hydrolytic acid, *i.e.* 58–76 % of its volume formed during the production of pigment titanium(IV) oxide.

The calculations show that utilization of hydrolytic sulphate acid by waste gases of burning furnaces of metatitanic acid paste is economically sound without any doubts.

The next stage of our investigations was the choice of apparatus for the hydrolytic sulphate acid evaporation and method of its dispersion.

The above- mentioned evaporation process may be carried out by two ways: (i) under the direct contact

between hydrolytic acid and waste gases and (ii) using the heating and evaporation of hydrolytic acid by waste gases by means of heat transfer through the wall [4-7]. The comparison of heat transfer factor, complicity of the main equipment and corrosion prevention, *etc.* shows that the first way has a row of advantages. Thus we used it.

The direct contact between gas and liquid phases may be realized in packed, film and hollow vessels by different ways. Using mass transfer vessels we need to take into consideration not only the heat transfer from gas to hydrolytic sulphate acid but two more factors: the transfer of TiO₂ dust from the gas phase to hydrolytic acid and salts (FeSO₄·nH₂O and others) crystallization. The latter two processes promote the blockage of packing in the apparatus; hence the mass transfer vessel for evaporation of hydrolytic acid by waste gases must be the hollow one.

The most effective hollow vessels are: vertical spray column and apparatus with liquid dispersion by mechanical devices. The latter ones, namely mass transfer apparatus with scoop-type dispersants, has better economic and technological indicators (energy specific consumption for dispersion, value of interfacial interaction surface, coefficients of mass- and heat transfer, *etc.*). However the presence of such roller details as dispersants or arbor sharply reduce the possibility of application of corrosion-resistant materials for their production (ceramics, plastic mass, fluoroplast). Taking into consideration all above-mentioned facts we recommend the hollow vertical spray column used for evaporating the hydrolytic acid.

2.2. Practical Part

2.2.1. Laboratory plant

The experiments were carried out at the laboratory plant the scheme of which is represented in Fig. 1. The evaporation process of hydrolytic sulphate acid was simulated under laboratory conditions and direct contact between gas (heat carrier) and acid and in the system hydrolytic acid drop – gas phase.

To simulate the waste gases we used wetted (0–22 vol %) and heated to 623–673 K air. For this purpose air was fed into the electric heater (2) by the compressor (8). The water steam from the evaporator (1) was added to air in the heater. The temperature in the heater (2) was reduced to the necessary value.

The air volumetric consumption was controlled by the rheometer (7). The water steam consumption was measured gravimetrically – by the difference between water mass in the evaporator (1) before and after the experiment. Then the value was calculated relatively to volumetric consumption of water steam. The intensity of

water evaporation of the evaporator (1) and the heating of air-steam mixture in the heater (2) was controlled by transformers (9) and (10), correspondingly.

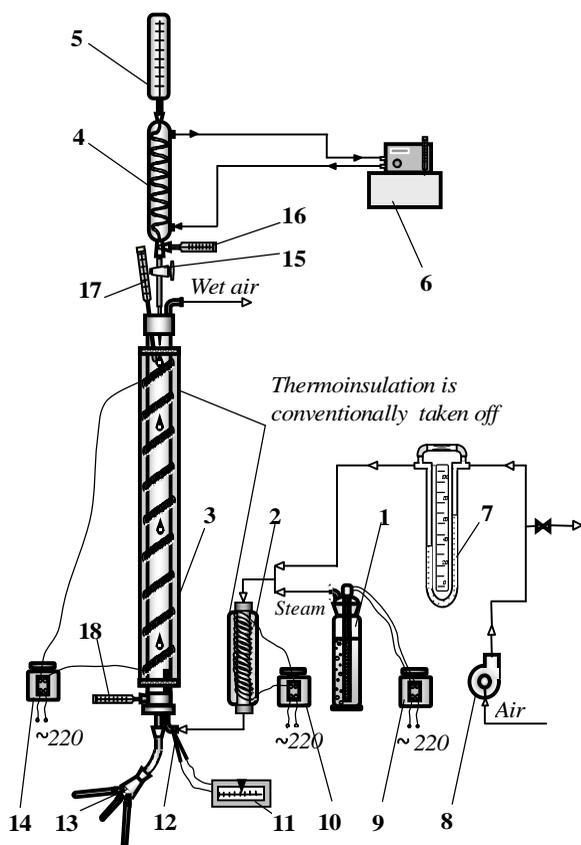


Fig. 1. The scheme of laboratory plant: water evaporator (1); electric heater of air-steam mixture (2); evaporating column (3); coiled heat exchanger (4); volumetric vessel (burette) (5); thermostat (6); rheometer (7); compressor (8); laboratory transformers (9, 10, 14); millivoltmeter (11); thermocouple (12); device for recovery of evaporated acid (13); measuring cock (15) and thermometers (16, 17, 18)

To prove the adequacy of simulated model of heat transfer process in the system gas-drop (sulphate acid) it is necessary to exclude the contact between the drop and evaporator surface, *i.e.* to ensure the possibility of heat exchange between acid and gas only under the condition of drop's free fall in the apparatus volume. Therefore for evaporation we used the vertical column, the working part was made of quartz tube, by the height of 950 mm and diameter of 43 mm (the working volume was 1.38 dm³). The solutions of sulphate acid were supplied by means of the capillary fixed vertically along the apparatus axis as a counterflow to the steam-gas mixture. The drops of evaporated acid got into the device for recovery of evaporated acid (13) without any contact with heated parts of the evaporating column. To compensate the heat losses

to the environment the heat was supplied to the quartz tube externally by means of nichrome spiral connected with power-supply source. The heat intensity was controlled by (14). The evaporating column was protected by casing (glass tube) and thermal insulation; it was equipped with connecting pipes for gas-steam inlet and outlet, as well as with branch pipes for thermometers and thermocouples.

Acid from the burette (5) after preheating in the heat exchanger (4) was fed by gravity to the column (3). The acid temperature was set by water thermostat (6) due to the continuous circulation of heat carrier in the secondary duct of heat exchanger (4). The temperature was controlled by the thermometer (16). The acid was fed dropwise; rate of the feed was controlled by a cock (15).

2.2.2. Experimental procedure and analyses

The solutions of sulphate acid of the necessary concentration and temperature were prepared previously. Then they were fed into the evaporating column with a necessary rate. The hot air-steam mixture was fed into the same column as a counterflow. The duration of acid efflux was fixed by a stop-watch. The acid concentrations before and after evaporation were determined using the acid-base titration.

To develop the technology and to calculate the main equipment it was necessary to investigate the effect of acid concentration change during the evaporation process on the boiling temperature and density. Evaporation was carried out in the open vessel; the temperature was measured by the mercurial thermometer; the density was determined using a density bottle. During the process the samples were withdrawn to determine the acid content using the titrimetry. The obtained results were compared with theoretical values for pure sulphate acid [8].

2.2.3. Methods of calculations

On the basis of experimental results we calculated the main indices of the heat transfer process – motive force (ΔT) and heat transfer factor (K_T).

To calculate the heat transfer factor from the gas to the drop surface it is necessary to determine the drop surface in the apparatus volume, gas and drop surface contact time and motive force of the heat transfer process. We accepted some theoretical assumptions, thus arguments on the basis of which the calculations were done are given below.

To calculate the drop surface we fixed the acid feed rate (I , drops/s), process time (t , s) and liquid volume fed for evaporation (V_{init} , m³). On the basis of mentioned data the calculations were done.

$$V_{drop} = \frac{V_{init}}{N}$$

We assumed that the drop has a spherical form. Thus,

$$V_{drop} = \frac{4pR^3}{3}; \quad R = \sqrt[3]{\frac{3V_{drop}}{4p}};$$

$$d_{drop} = 2R; \quad S = p \cdot d_{drop}^2$$

To calculate the drop and heat carried (gas) contact time we assumed that the drop motion is uniformly accelerated in the apparatus. It is known from [2, 3] that the rate of the drop motion ranged from 1.5 to 1.9 m/s for the particles with the diameter of 2–3 mm. Thus we assumed that $W_{fin} = 1.9$ m/s.

The average rate of the drop flight in the evaporating column is calculated as arithmetical mean ($W_{av} = 0.95$ m/s):

$$W_{av} = \frac{W_{init} + W_{fin}}{2} = \frac{0 + 1.9}{2} = 0.95$$

The contact time (τ , s) is:

$$t = \frac{H}{W_{av}} = \frac{0.95}{0.95} = 1 \quad (1)$$

where H is the height of the column working part, m.

To determine the motive force of the process we measured the temperatures of gas and liquid phases at the inlet and outlet of the column. The motive force is calculated by the formula (2)

$$\Delta T = \frac{\Delta T_{inlet} - \Delta T_{outlet}}{2.31g \frac{\Delta T_{inlet}}{\Delta T_{outlet}}} \quad (2)$$

where ΔT_{inlet} is the difference between gas and acid temperatures at the inlet to the column; ΔT_{outlet} is the difference between gas and acid temperatures at the outlet.

The amount of heat spent for water evaporation from the drop:

$$Q = r_{H_2O} \cdot m_{H_2O}^{ev} \quad (3)$$

where $m_{H_2O}^{ev}$ is the evaporated water mass, kg; r_{H_2O} is the latent heat of water evaporation, kJ/kg

The mass of evaporated water was determined by two methods:

a) directly by initial and finite masses of the sulphate acid solution

$$V_{drop}^{ev} = \frac{V_{init} - V_{fin}}{N} \quad (4)$$

$$m_{H_2O}^{ev} = V_{drop}^{ev} \cdot \rho \quad (5)$$

where ρ is density, kg/m³

b) by concentrations of sulphate acid before and after evaporation

$$V_{fin} = \frac{C_{init} \cdot V_{init}}{C_{fin}} \quad (6)$$

Then the calculations are the same as in a previous case.

The values of evaporated water mass calculated by different methods are in agreement; therefore we took the averaged value to calculate the heat transfer factor.

The heat transfer factor (K_T , kJ/(m²·s·K) or kW/(m²·K)) is calculated using the formula (7)

$$K_T = \frac{Q}{S \cdot t \cdot \Delta T} \quad (7)$$

3. Results and Discussion

The sulphuric acid drop increases its concentration by 1.5–3.5 % flying the distance of 0.95 m. In the industrial column the distance of drop flight in the gas stage will increase in two or three times. Obviously the H₂SO₄ concentration in hydrolysis acid will increase by 4–8 % for the single passing through the column.

Dependence of heat transfer factor on the process motive force at different values of H₂SO₄ concentration in the acid is shown in Fig. 2. The increase of the motive force (ΔT) increases the heat transfer factor. This fact is in a good agreement with general postulates of heat exchange, since the gas phase around the drop is turbulized with the increase in temperature difference between the drop and gas (the thickness of gas film decreases). The results are the improvement of heat emission from gas to the drop and the increase of heat transfer factor.

As it was expected, the decrease of H₂SO₄ concentration in the sulphate acid increases the heat transfer factor. Thus, the decrease of H₂SO₄ concentration from 52.7 to 28.5 % at $\Delta T = 110$ K increases K_T from 0.07 to 0.25 kW/(m²·K). The reasons are both the decrease of acid viscosity and the increase of water steam partial pressure over the acid due to its dilution. In other words, the mass transfer affects the heat transfer process. The experimental results given in Fig. 3 confirm this fact.

One can see from Fig. 3 that the increase of moisture content in the gas phase decreases the heat transfer factor. Thus, at H₂O content of 10 vol % in the gas $K_T = 0.47$ and at 25 vol % – only 0.33 kW/(m²·K), *i.e.* due to the increase of H₂O partial pressure the rate of water evaporation from the drop surface decreases. The result is retardation of heat transfer rate.

The motive force of the mass transfer is a difference between water steam partial pressure over sulphate acid and its partial pressure in the gas phase. At low content of water steam in the gas and relatively great difference between rates of the drop and gas phase movement the evaporation process is limited by the rate of heat supply to the drop and does not depend upon the rate

of water steam removal from its surface. The higher moisture content, the greater influence of water steam removal on the evaporation process. The steam film is formed around the drop, preventing the heat transfer, *i.e.* the decrease of mass transfer intensity decreases the heat transfer factor.

For theoretical grounds of the concentration process of hydrolytic sulphate acid, namely at the stage of material and heat calculations, the changes of acid density and boiling temperature during evaporation are the important factors. Due to the theory, the boiling temperature of the solution is higher than that of the solvent by the value of

temperature depression. Since the initial solutions of hydrolytic sulphate acid are complex multicomponent system, the change of quantitative and qualitative composition, as well as a phase stage of the mixture components, may be expected during water evaporation. At the first approximation, ignoring all impurities except FeSO_4 (which content is insignificant, less than 0.5 mas %), we may assume that the mentioned solution is a three-component system: $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$. That is why we determined the effect of concentration change of hydrolytic sulphate acid on the density during evaporation and compared obtained results with theoretical values.

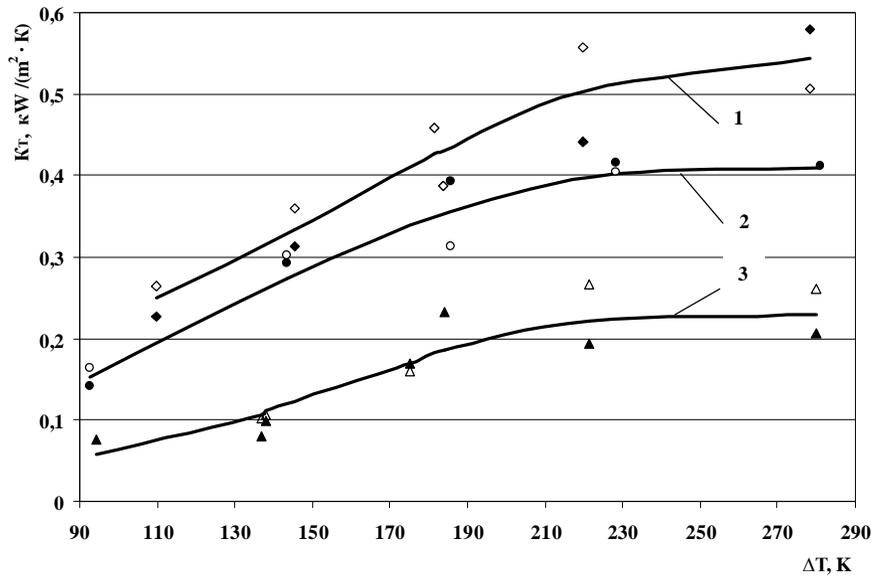


Fig. 2. Dependence of heat transfer factor on the motive force of heat exchange process and sulphate acid initial concentration (%): 28.5 (1); 37.4 (2) and 52.7 (3). The gas initial humidity is 18 vol %

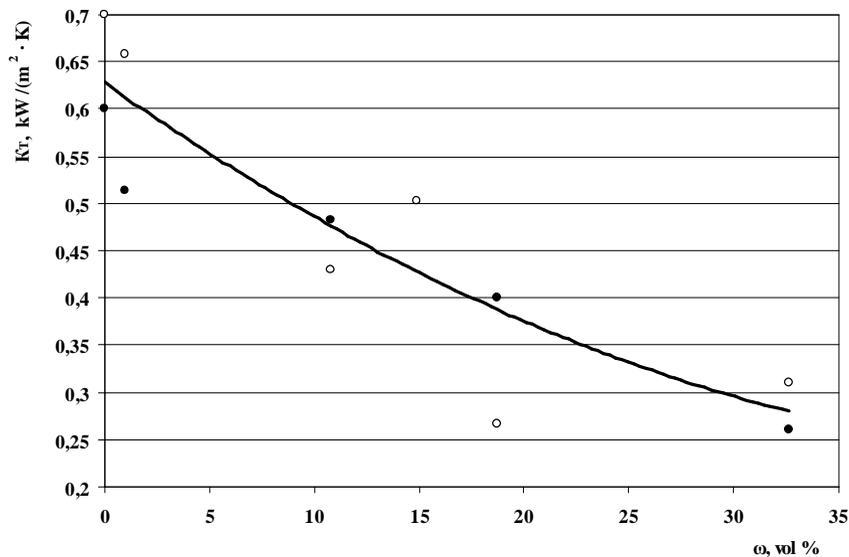


Fig. 3. Dependence of heat transfer factor on air moisture content. The initial concentration of sulphate acid is 28.5 %, motive force is 458 K

The change of pure solutions boiling temperatures (curve 1) and solutions of hydrolytic sulphate acid (curve 2) is shown in Fig. 4. The boiling temperature within the concentration range of hydrolytic sulphate acid of 35–55 mas % essentially differs from the theoretical value for pure sulphate acid. As it was expected, the increase of acid concentration during evaporation increases the boiling temperature of the solution but at the concentration of $\approx 39\%$ the intensity of increase descends. The reason is that on reaching 39 % concentration of the acid in the system $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ the nuclei of $\text{FeSO}_4\text{-H}_2\text{O}$ crystals are formed. Then the monohydrate of ferrum(II) sulphate precipitates as a result of desalting effect and decreases the concentration of Fe^{2+} and SO_4^{2-} ions. In accordance with the theory the decrease of solution concentration decreases the boiling temperature.

However the mass content of sulphate acid in the system is higher by order than ferrum(II) sulphate concentration, therefore the general tendency of boiling temperature growth is preserved during evaporation. During the concentration process of hydrolytic sulphate acid, at the concentration $> 50\%$, its boiling temperature is almost the same as the temperature of pure sulphate acid (curve 1). The slight deviation from theoretical data is explained by the minor residual content of impurities in the evaporated hydrolytic sulphate acid.

The investigations concerning the effect of acid concentration on its density (Fig. 5) show that during concentration process the solution density increases, achieves the maximum value of 1528 kg/m^3 (at the concentration of 45 mas %), sharply decreases to 1370 kg/m^3 at the concentration of 50 mas % and then increases again.

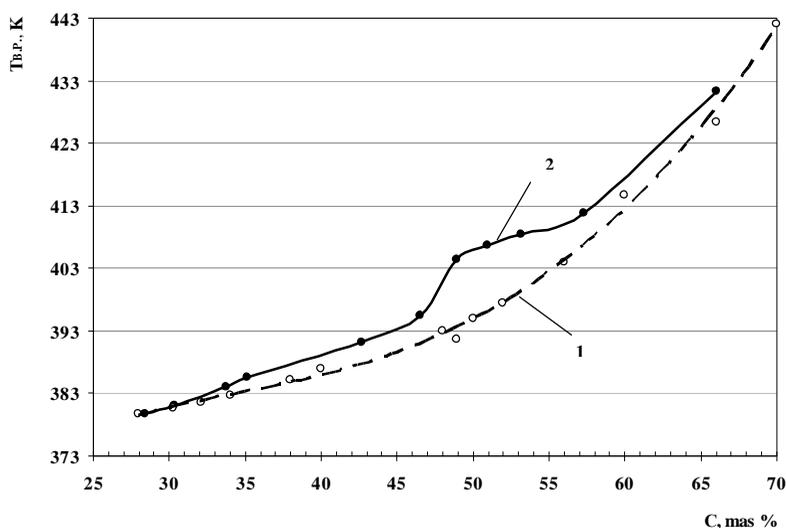


Fig. 4. Dependence of the boiling temperature of hydrolytic sulphate acid upon its concentration during evaporation: solution of the pure sulphate acid (1) and solution of the hydrolytic sulphate acid (2)

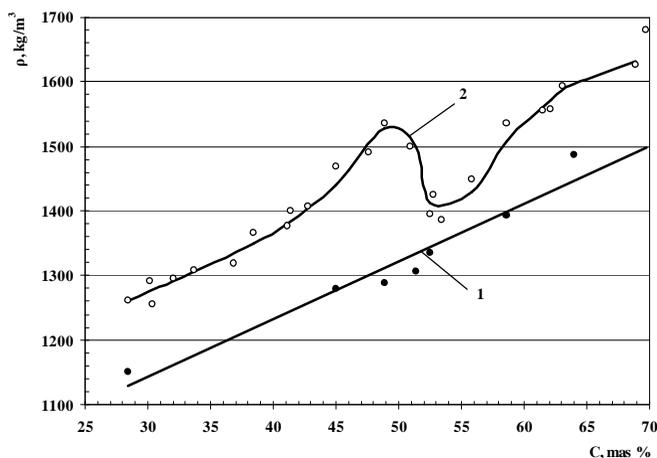


Fig. 5. Dependence of the hydrolytic sulphate acid density upon its concentration during evaporation: solution of the pure sulphate acid (1) and solution of the hydrolytic sulphate acid (2)

The sharp increase of hydrolytic sulphate acid density in the area of concentrations 39–45 % indicates the new phase forming in the system $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$. Here the solution oversaturation takes place followed by the formation of microscopic nuclei of $\text{FeSO}_4\text{-H}_2\text{O}$ crystals. In other words the fine suspension is formed. Theoretically the suspension density may be calculated by the following formula:

$$\frac{1}{r_s} = \frac{c}{r_{sol}} + \frac{1-c}{r_l} \quad (8)$$

where r_s is a suspension density, kg/m^3 ; r_{sol} is a solid phase density, kg/m^3 ; r_l is a liquid phase density, kg/m^3 and c is a mass part of the solid phase in the suspension, parts.

From Eq. (8) we see that the sharp increase of suspension density is a result of solid phase appearance with the high density, as well as the increase of its part.

The further concentration of the solution leads to the increase of $\text{FeSO}_4\text{-H}_2\text{O}$ crystals. After achieving the definite sizes, they precipitate under the gravity. Consequently, the part of solid phase in suspended state decreases and the density of hydrolytic sulphate acid decreases too in the area of concentrations 45–50 mas %. Then the density fluently increases and the deviation of values from theoretical data (curve 1) is explained by residual content of impurities in the evaporated hydrolytic sulphate acid.

The formation of $\text{FeSO}_4\text{-H}_2\text{O}$ solid phase at intermediate concentrations of sulphate acid may complicate the technological process (blocking of jets and supply pipelines). Therefore it is advisable to carry out the evaporation process with intermediate extraction of solid phase.

4. Conclusions

1. Waste gases from burning furnaces of metatitanic acid paste at the production of pigment titanium(IV) oxide contain the great amount of energy and may be used for evaporation of hydrolytic sulphate acid obtained at such production.

2. Due to the energy of waste gases 58–76 % of waste hydrolytic sulphate acid may be utilized.

3. We recommend a hollow vertical spray column as a main apparatus for evaporation of hydrolytic sulphate acid.

4. The experimental results confirm that the evaporation intensity is high under the direct contact between waste gases and acid. On the basis of determined heat transfer factor the sizes of evaporating column and jets, the number of jets and other calculations have been done.

5. The evaporation process of hydrolytic sulphate acid is advisable to carry out with intermediate extraction of formed solid phase of monohydrate ferrum(II) sulphate.

References

- [1] http://www.titanexport.com/index_rus.html
- [2] Skomorokha V., Zarechnyi V., Vorobieva I. and Vakal S.: Proizvodstvo Dvukisi Titana Pigmentnogo Sulphatnym Sposobom. ATZT "Arsenal-Press", Sumy 2002.
- [3] Dyumaev K., Elbert E., Sushchev V. and Perfiliev V.: Regeneraciya Otrabotannykh Sernokislotnykh Rastvorov. Khimiya, Moskva 1987.
- [4] Shvydkyi V. and Ladygichev M.: Ochistka Gasov. Teploenergetik, Moskva 2002.
- [5] Aliev G.: Tekhnika Pyleulavlivaniya i Ochistki Promyshlennykh Gasov. Metallurgiya, Moskva 1986.
- [6] Mikhaileenko G.: Novye Raspylivayushchie Ustroystva v Sistemakh Promyshlennoi Pylegazoochistki. Astroprint, Odessa 2008.
- [7] Golovachevskiy Yu.: Orositeli i Forsunki Skrubberov Khimicheskoi Promyshlennosti. Mashinostroenie. Moskva 1974.
- [8] Malin K. (Ed.): Spravochnik Sernokislotchika. Khimiya, Moskva 1971.
- [9] Pavlov K., Romankov P. and Noskov A.: Primery i Zadachi po Kursu Processov i Apparotov Khimicheskoi Technologii. Khimiya, Moskva 1987.

УПАРЮВАННЯ ГІДРОЛІЗНОЇ СУЛЬФАТНОЇ КИСЛОТИ ВІДХІДНИМИ ГАЗАМИ ПЕЧЕЙ ПРОЖАРЮВАННЯ ПАСТИ МЕТАТИТАНОВОЇ КИСЛОТИ

Анотація. Теоретично обґрунтовано і практично підтверджено доцільність упарювання гідролізної сульфатної кислоти відхідними газами печей прожарювання пасту метатитанової кислоти. Встановлено оптимальний режим та розраховано масообмінний апарат процесу упарювання. Експериментально підтверджено високу інтенсивність такого процесу. Встановлено вплив рушійної сили процесу та вологовмісту відхідних газів на коефіцієнт теплопередачі.

Ключові слова: гідролізна сульфатна кислота, відхідні газу.