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Optimization of Process Parameters of Waste SO_2 Utilization from Titanium White Manufacture

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Abstract

An absorption process of SO_2 in the aqueous suspension of ilmenite has been found to be an efficient process of gas desulphurization. Practically, the complete absorption of SO_2 is possible at the appropriate selection of the principal process parameters: ilmenite content in the suspension, and temperature.

Keywords: ilmenite, SO_2 utilization, catalysis in solution.

Introduction

Ilmenite is a basic raw material for titanium white (TiO_2) manufacture by the sulphate process [1]. It is the complex mineral based on iron (II) metatitanate – $FeO \cdot TiO_2$. Ilmenite concentrate usually contains ca. 40% TiO_2 and the admixture of oxides of variable valency metals such as Mn, Cu, Cr, and V, as well as other metals: Mg, Ca, Al.

The chemical conception of a gas desulphurization process from TiO_2 manufacture has been formulated on the basis of preliminary studies [2], assuming the absorption of waste SO_2 in the aqueous suspension of ilmenite. According to this concept, the process run is highly complex. In the first, the main stage proceeds the absorption of SO_2 and O_2, contained in a waste gas, followed by the catalytic oxidation of SO_2 in the solution:

$$SO_2 + 1/2\ O_2 + H_2 \xrightarrow{Me^{n+}} H_2SO_4 \qquad (1)$$

The catalytic agents for this reaction are ions (Me^{n+}) of variable valency metals [3]. Ions of manganese, copper, iron, chromium and cobalt are mentioned as the most active catalysts [4-6].

In the investigated process, a catalyst of the reaction (1) are Fe ions, whose catalytic activity is intensified by ions of the other variable valency metals contained in ilmenite.

In the subsequent process stage the formed sulphuric acid reacts with the ilmenite components:

$$FeO \cdot TiO_2 + 2H_2SO_4 \rightarrow FeSO_4 + TiSO_4 + 2H_2O \qquad (2)$$

$$Me_mO_n + nH_2SO_4 \rightarrow Me_m(SO_4)_n + nH_2O \qquad (3)$$

It should be pointed out that reactions (2) and (3) also proceed during the solubilization of ilmenite in concentrated H_2SO_4 in the TiO_2 manufacture process. It was assumed that a mixture, after SO_2 absorption, would be further treated in the titanium white manufacture plant. Therefore, the investigated process of the gas desulphurization is based on the raw materials used for TiO_2 manufacture, which does not lead to the formation of wastes and allows saving of some amounts of H_2SO_4 in the titanium white manufacture process.

Preliminary studies [2] have found that the parameters which have a decisive influence on the SO_2 absorption progress are the ilmenite content in the suspension, and temperature. As a result of the monofactorial design procedure it has been established that good conditions for the process operation are achieved at ilmenite content of 60 g/dm^3 and a relatively high temperature – 80°C, or 50°C and ilmenite content of 140 g/dm^3.

It was assumed that the process should not be intensified by a significant increase of these parameters. This particularly concerns temperature, which determines the level of energy consumption. Therefore, the effects of both parameters on SO_2 absorption has been studied using the extreme experiment design procedure [7, 8].

Experimental

Ilmenite concentrate containing 43.96% TiO_2; 41.1% Fe; and 5.7% Fe_2O_3 was employed in the experiments. The remainder was an admixture of oxides of metals such as Cu, Mn, Cr, and V, as well as Ca, Mg and Al. A fraction with the grain diameter $\leq 10^{-3}$ m was used.

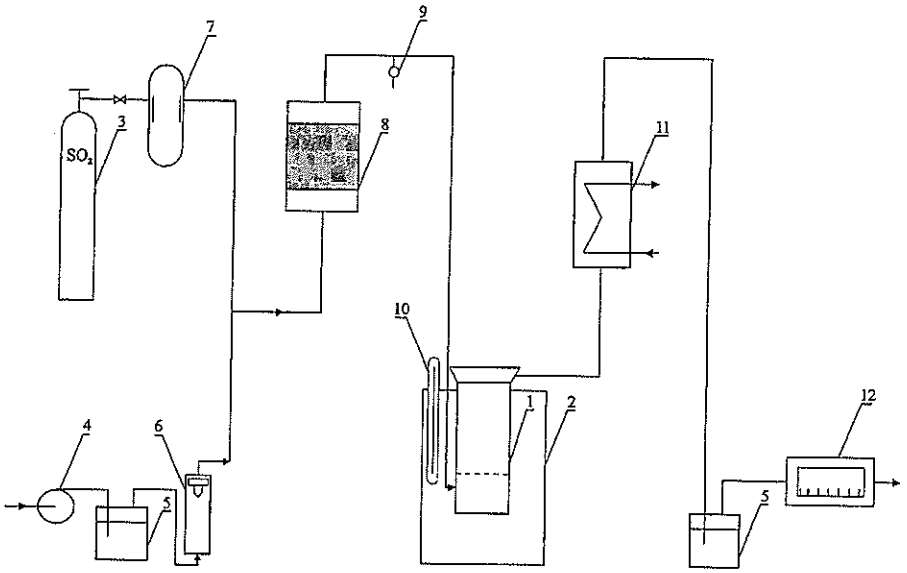


Fig. 1. Schematic diagram of apparatus for the absorption of SO_2; 1 – reactor with stirrer, 2 – ultrathermostat, 3 – gas cylinder with SO_2, 4 – air metering pump, 5 – washer filled with granular $CaCl_2$, 6 – rotameter, 7 – fleometer, 8 – gas mixer, 9 – valve for gas sampling, 10 – thermometer, 11 – reflux condensor, 12 – SO_2 analyzer

The absorption and oxidation of SO_2 was studied using the experimental system shown in Figure 1. Air, dried in a washer containing $CaCl_2$, along with SO_2 from a gas cylinder, entered the mixer and then a reactor. The barbotage reactor with a glass sinter grate and stirrer with an inner diameter of d=50 mm was used. The volumetric flow rate of the gases was measured using a fleometer and a rotameter. The post-reaction gas escaped from the reactor through a reflux condenser placed above it, which prevented a change of volume and solution concentration as a result of water evaporation. It was then directed to a drying washer with $CaCl_2$ and then to SO_2 analyzer. The analyzer used an Infratyt IV recorder, permitting continuous recording of the concentration changes in the effluent. The gas sampling valve was placed beside the gas mixer to perform the control chemical analyses.

The degree of SO_2 concentration in the gas at the reactor inlet and outlet was taken as a criterion for the process evolution:

$$\alpha_{SO_2} = \frac{C^o_{SO_2} - \bar{C}_{SO_2}}{C^o_{SO_2}}$$

where:

$C^o_{SO_2}$ – constant concentration of SO_2 at inlet

$$\bar{C}_{SO_2} = \frac{1}{t}\int_0^t C_{SO_2}\,dt$$ – average concentration of SO_2 at outlet

t – time of reaction.

Results and Discussion

Two series of the experiments were performed, the results of which are presented in Figures 2 and 3. The experimental design and the values of the degree of SO_2 absorption (α_{SO2}) are shown in Tables 1 and 2.

It was initially assumed (series I), that the temperature on the fundamental level amounts to 40°C and the ilmenite content in the suspension – 40 g/dm^3 . The interval of temperature changes was assumed a priori $\Delta X_1 = 5$°C, whereas for ilmenite content it was $\Delta X_2 = 10$ g/dm^3.

Treating both parameters as independent variables of a function $y = \alpha_{SO2}$ and denotating as X_1 – temperature, as X_2 – the ilmenite content in the suspension, they are coded in the following manner:

$$x_1 = \frac{X_1 - 5}{5} \qquad x_2 = \frac{X_2 - 40}{10}$$

The full factorial experiment of a type 2^n has been realized. The experiments were performed with the SO_2 content of 0.3 vol% in the gas. The rate of gas flow amounted to 50 dm^3 /h STP, the reaction mixture volume – 0.25 dm^3 and the frequency of stirrer revolutions – 10s^{-1}.

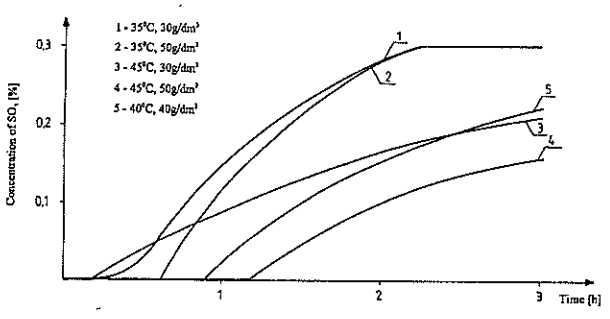


Fig. 2. Effect of temperature and ilmenite content in the aqueous suspension on the degree of SO_2 absorption (I series of the experiments)

Table 1. Plan and the experimental results of I series.

Investigated parameters	Temperature	Ilmenite content in the suspension	Degree of absorption
	[°C]	[g/dm³]	$\bar{\alpha}_{SO_2}$ [%]
Fundamental level $x_i = 0$	40	40	
Range of variations	5	10	
Higher level $x_i = +1$	45	50	
Lower level $x_i = -1$	35	30	
	Code symbols of variables		
	x_1	x_2	
Experiment 1	−1	−1	36.95
Experiment 2	−1	+1	41.55
Experiment 3	+1	−1	60.25
Experiment 4	+1	+1	80.92
Experiment 5	0	0	68.60

Assuming that the central point of a plan, determined by the coordinates at fundamental level, is placed at a distance from the extreme of a function $y = \alpha_{SO_2}$, the dependence of y from both parameters can be approximately described by the linear equation [7]:

$$y = b_o + b_1x_1 + b_2x_2$$

The coefficients of this equation, calculated by the least-squares method after accomplishing series I, are as follows:

$$b_o = 54.92 \qquad b_1 = 6.43 \qquad b_2 = 6.32$$

The determination coefficient (second power of the correlation coefficient) amounts to $R^2 = 0.93380$. The significance of the observed effects was determined using test F Fisher - Snedecor. The value of variable F for the significance level of $\alpha = 0.05$ – read over from the statistical tables – amounts $F_\alpha = 7.7086$. The calculated value of variable $F_C = 19.740$.

The above values indicate a good fitting of the equation with the experimental data. The value of R^2 indicates that 93.8% of analyzed variable was explained. Because $F_C > F_\alpha$ on the level of $\alpha = 0.05$, it can be concluded that the linear effect is highly significant. This thesis can be stated with a 5% probability of error commitment.

The values of the b_1 and b_2 coefficients are equal to the corresponding partial derivatives of the function $y = \alpha_{SO_2}$. They determine the direction and magnitude of the changes of both parameters for the subsequent series of experiments.

Since both derivatives have the positive sign (from the regression equation results), in order to obtain more and more higher values of degrees of SO_2 absorption, it is necessary to increase simultaneously temperature and ilmenite content in relation to the values on the fundamental level. According to the Box-Wilson method [7], and based on the calculated values of b_i, the intervals of changes (incremental of the parameter values) can be determined for the following experimental series:

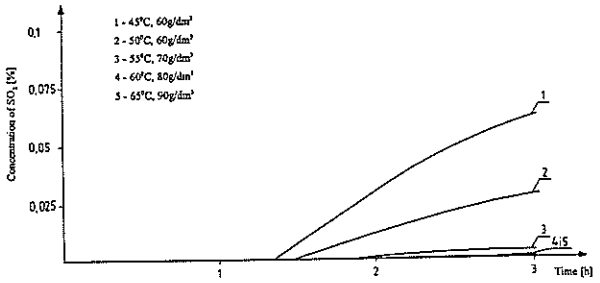


Fig. 3. Effect of temperature and ilmenite content in the aqueous suspension on the degree of SO_2 absorption (II series of the experiments)

$$\Delta X'_1 = b_1 \cdot \Delta X_1 = 6.43 \cdot 5 = +32.2°C$$

$$\Delta X'_2 = b_2 \cdot \Delta X_2 = 6.32 \cdot 10 = 63.2 \text{ g/dm}^3$$

These increments were too large; however, they can be changed to a lesser degree, preserving the ratio between them:

$$\frac{\Delta X'_2}{\Delta X'_1} = 1.975$$

Moderately assuming that $\Delta X_1 = +5°C$, a value of $\Delta X_2 = +9.879$ g/dm³ will be obtained. In the subsequent series of the experiments the interval of changes have been taken for temperature – 5°C, whereas for ilmenite content – 10 g/dm³.

The data presented in Table 2 shows that a shift towards the extreme (maximum) of the function $y = \alpha_{SO_2}$, which was obtained by the addition to the parameter values of the

Table 2. Plan and the experimental results of II series.

Investigated parameters	Temperature	Ilmenite content in the suspension	Degree of absorption
	[°C]	[g/dm³]	$\bar{\alpha}_{SO_2}$ [%]
Ivestigated level	40	40	68.60
Range of variations	+ 5	+ 10	
Experiment 1	45	50	80.92
Experiment 2	50	60	93.77
Experiment 3	55	70	97.37
Experiment 4	60	80	99.82
Experiment 5	65	90	97.90

corresponding increments. It can be seen that in II series of the measurements, the coordinates of the measurement points are placed in the steady-state area of the process parameters.

Both the temperature and ilmenite content in the suspension have a significant effect on the SO_2 absorption process. Initially, with a simultaneous increase of both parameters, and with the preservation of the calculated ratios between them, the degree of absorption increases to 99.82%. Further increment of the value causes the deterioration of SO_2 absorption, which is probably connected with a decrease of solubility of the gaseous reagents (particularly O_2) in the absorption solution at higher temperatures. Therefore, it can be concluded that the process should be carried out at about 60°C and ilmenite content in the suspension should be about 80 g/dm^3. It is worth mentioning that practically the complete SO_2 absorption can be obtained at the reduced values of the parameters in relation to the values based on the monofactorial experiments.

Conclusions

SO_2 absorption in the aqueous suspension of ilmenite is a very effective process for removing SO_2 from waste gases generated during titanium white manufacture. An appropriate selection of the main process parameters (ilmenite content in suspension, and temperature) enables us to obtain high values of the absorption degree, up to nearly 100% with their moderate values – 80 g/dm^3, 60°C. It is also essential that this process be based on the raw materials utilized in the TiO_2 manufacture and does not lead to the formation of wastes difficult for disposal, which is the case in many processes of gas desulphurization used on a commercial scale.

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