

UTILIZATION OF PIGMENT TITANIUM (IV) OXIDE IRON-CONTAINING INDUSTRIAL WASTE

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Abstract: To solve the problems of utilization of large-tonnage wastes from of titanium (IV) oxide production, which is Fe (II) sulphate, it is suggested to use number of production technologies of large-tonnage productions, such as mineral fertilizers, iron ore pellets, active admixture to cement production, inorganic pigments. By this way it is planned to avoid completely the ecological risk from these waste impact.

Keywords: Fe (II) sulphate, titanium (IV) oxide, utilization, chemical fertilizers, pellets, active admixture to cement, pigment.

INTRODUCTION

The development of titanium (IV) oxide production, which appears to be a valuable chemical product that is used not only in Ukraine's industry but also is exported to more than 50 countries of the world, is accompanied by the industrial waste accumulation - is Fe (II) sulphate. Today this product is used only for inorganic pigments production, which are of low quality and are not widely used, this waste is also used in small volumes for coagulators production, the test production run of which is used in cement industry. But these small volumes of its use do not solve the problems of its utilization, that is why the major quantity of it goes to industrial waste landfill. Today the volume of the waste equals more than 1 million ton in "Sumyhimprom" public corporation and more than 2 million ton in "Tytan" national corporation (Armyansk city, Crimea). In Sumy city the landfill occupies 1.2 hectare of plough-land, in Crimea half of the landfill is situated in coastal zone of Syvash gulf and in the gulf in particular. The waste contains a considerable quantity of free sulphuric acid which with the ground water and the water from Syvash gulf is spread on the hundreds hectares of land, by this way salting them, changing the soil structure, polluting by the titanium and chromium ions which are contained in the waste. Taking into consideration that in this paper the issues of this waste complex utilization by the way of perspective technologies introduction are covered [1], and as the result of their realization the valuable products are manufactured and at the same time it contributes to minimizing the ecological risk from these waste.

RESULTS AND DISCUSSION

Mineral fertilizers production

The two variants of fertilizer production technology were considered (Figure 1) [2]:

1. Mixing of the components in such order: the waste → phosphorite → ammonia water.
2. Mixing of the components in such order: the waste → ammonia water → phosphorite.

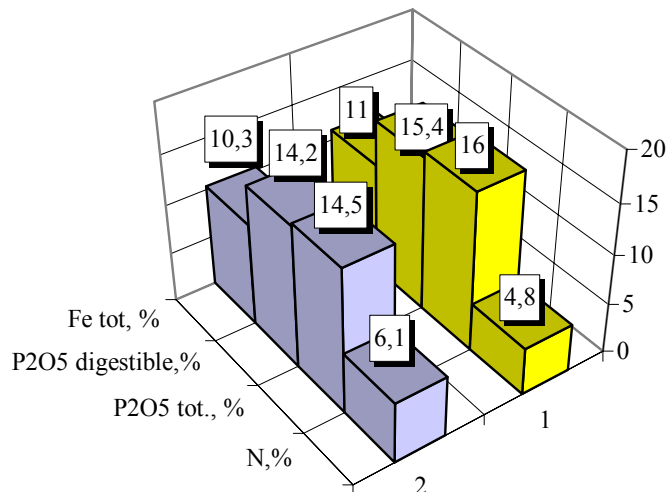


Figure 1. The content of nutrition units in the fertilizers depending of the fertilizer synthesis method.

It was determined that in the first case a free acid that is contained in the waste was used on partial splitting of the phosphorite, which increases the content of P_2O_5 water-soluble form and the ammonia water is used to neutralize residual acidity. That is why, comparing to the second option, in these fertilizers the content of P_2O_5 water-soluble form is increased and the content of ammonium sulphate is decreased. The disadvantage of this method is a partial acid use on the reaction with carbonates which are contained in a phosphoric ore.

For the second option the free acid of the waste is used in the reaction of forming ammonium sulphate, a phosphorite powder is added as unit of a fertilizer mechanical mixture. For this type of fertilizer the increased content of ammonium sulphate and the decreased content of P_2O_5 water-soluble form appear to be typical.

The first stage in both technologies is waste dissolving in water. To establish the kinetics of Fe (II) sulphate dilution, and the optimal temperature selection for the process realization there were examinations conducted and their results are presented in Figure 2.

Analyzing the experiment data (Figure 2) we took the optimal condition of process realization the temperature of 323 K. In this temperature Fe (II) sulphate is dissolved during 35–40 min. As it is seen from the Figure 3, there is no purpose to take the lower temperature, because it enlarges the process duration. The higher temperature is also unreasonable, because it enlarges the energy consumption, and the second stage of the process (the interaction between the solution and phosphorite) takes place in the temperature 323 K, that is why there is no reason to increase the temperature of Fe (II) sulphate dissolving.

In the case of the first technology variant realization, tunis phosphorite was added to the received Fe (II) sulphate solution, rating 1 mass part of phosphorite to 1 mass part of iron vitriol. The mash was kept during 1 hour in the temperature 323 – 328 K in the conditions of it's continuous stirring. It was noticed the light CO₂ discharge, which appears to be an evidence of interaction between free sulphate acid, which is contained in iron vitriol, and the components of phosphate crude.

The mash result analysis shows that the chemical interaction practically did not touch phosphate part of the phosphorite. At the same time the part of Fe is transformed in insoluble form, which is an evidence of interaction between the part of Fe (II) sulphate with carbonates.

The received mash is neutralized by ammonia water until pH = 9. In the process of ammonization there were not noticed mash foaming or sprinkling. The neutralized mash is movable, the colour is black.

The neutralized mash goes to drying.

In the case of the second technology variant realization, after vitriol dissolving its neutralization was carried out by ammonia water. The neutralization kinetics is presented on the Figure 3.

It can be seen from the Figure 3 that the neutralization till pH = 8,6 is performed in the condition of adding 250 ml of ammonia water (for the conditions of the experiment). By the way of balance calculation it was established that for the conditions of industrial production is amounts to 740 l/ton of Fe (II) sulphate.

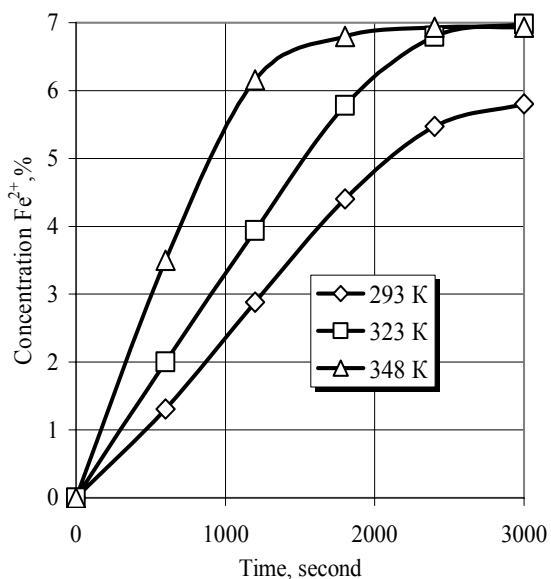


Figure 2. The kinetics of Fe (II) sulphate dilution in a distilled water.

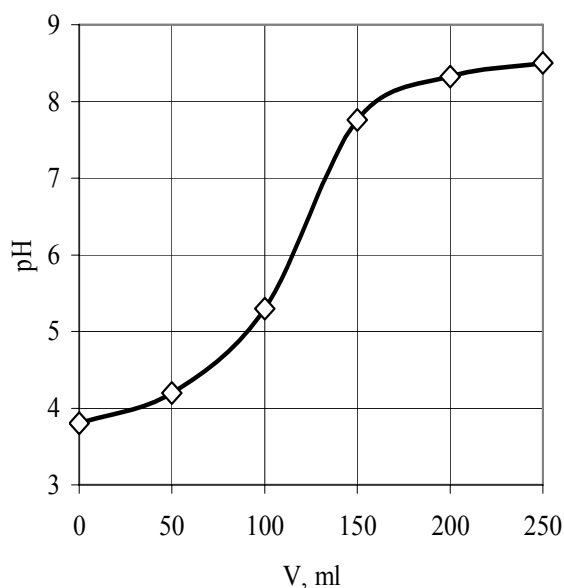


Figure 3. The impact of ammonia water inputs of neutralized mash pH.

To the neutralized mash, which contains ammonium sulphate and iron compounds Fe⁺³, Fe⁺² with the ratio of Fe_{total} :SO₄ = 1:3,15, was loaded not-milled tunis phosphorite with approximate phosphorite mass input: 1 mass part of phosphorite to 1 mass part of iron vitriol. In the process of

technological mediums mixing there was formed dense movable mash which does not need any additional dilution with water and does not split on layers.

The data from process laboratory experiments allowed to perform the industrial test of the technology on the technological capacity of “Sumyhimprom” public corporation. In total 153 ton of the product were produced, which satisfied the technological task about its content.

The production of active admixture to cement

The main requirement to the cement admixtures is their granulation, because it simplifies the conditions of storing, transportation and their proportioning to clinker mill. To use the titanium (VI) oxide production waste, which is Fe (II) sulphate, it is important to follow the 2 main requirements:

1. to neutralize the excess of sulphate acid by loading the admixture;
2. to obtain the needed granules strength.

We have examined the two options of loading the neutralizing granules-making admixture to the waste content:

1. Loading of chamotte and kaolin powder (CKP).
2. Loading of milled chalk.

The laboratory experiment in order to receive the active admixture was carried out in such order: monohydrogen vitriol (or the mixture of monohydrogen and 7-hydrogen vitriol in the indicated ratios) was neutralized by the admixture, taken in the calculated quantity, the received bland was kept in indoor temperature during 5 days until the complete neutralization, and then it was granulated and dried. The granulation was made in the laboratory granulator. To perform this, the water was added to the balanced bland in a quantity that provides the process of granules rolling. The received wet granules were dried to a constant mass. The research temperature was determined experimentally.

The experiment results (production of the active admixture on the base of the mixture of monohydrogen and 7-hydrogen vitriol and the neutralizing adding – CKP and chalk) are presented in a Table 1.

On the basis of the carried out investigation data we can conclude that:

- 1) Using the current technology without any significant changes it is impossible to receive the granular admixture with Fe (II) content less than 19%.
- 2) During the basic material preparation stage loading of the bivalent Fe salt (and 7-hydrogen vitriol) as an additional Fe (II) source which allows to increase Fe (II) content in the end product until 20% and higher and also to decrease free acidity of the whole mixture which goes to neutralization.
- 3) The substitution of chamotte and kaolin powder neutralizing mixture with natural milled chalk allows to increase Fe (II) content in the end product until 22%.

Table 1

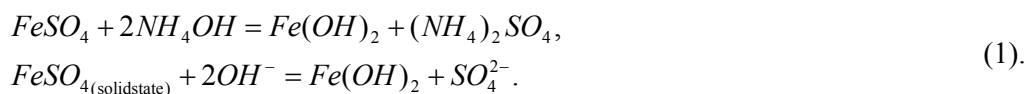
Mixture content		t°C	Index names and units of measurement, %				
FeSO ₄ xH ₂ O:FeSO ₄ x7H ₂ O	Vitriol : CKP		Fe _{total}	Fe ²⁺	Fe ³⁺	TiO ₂	H ₂ SO ₄ quantitative
“Control study” FeSO ₄ xH ₂ O 3:1		80 130	15,8 17,8	14,2 15,9	1,6 1,9	1,4 1,8	-
1:1	6:1	80 130	21,7 24,1	20,8 22,9	0,9 1,2	0,8 1,2	-
2:1	4:1	80 130	19,3 20,0	18,2 19,1	1,2 1,6	1,2 1,6	0,7
2:1	6:1	80 130 150 200	21,4 21,4 21,6 21,8	19,5 20,0 20,2 20,4	1,9 1,4 1,4 1,4	1,4 1,3 0,95 1,1	1,2 1,0 0,75 0,34
Mixture content		t°C	Index names and units of measurement, %				
FeSO ₄ xH ₂ O:FeSO ₄ x7H ₂ O	% chalk adding		Fe _{total}	Fe ²⁺	Fe ³⁺	TiO ₂	H ₂ SO ₄
“Control study” FeSO ₄ xH ₂ O 150 % stoichiometry		80 130	14,8 16,9	13,7 15,8	1,1 1,1	1,4 1,8	-
1:1	150% stoichiometry	80 130	21,0 23,3	19,7 22,1	1,3 1,2	1,2 1,5	-
2:1	150% stoichiometry	80 130	20,3 21,6	19,3 20,1	1,0 1,4	1,5 1,6	0,1
2:1	100% stoichiometry	80 130 150 200	24,0 23,8 23,7 22,9	22,7 22,6 22,5 21,8	1,3 1,2 1,2 1,0	1,4 1,1 1,4 0,9	1,4 1,3 0,6 0,2

Pellets production

The main technological stages of waste processing are the following:

- 1) magnetite synthesis;
- 2) end product extraction from the reaction mixture;

To receive magnetite the part of Fe²⁺ ions should be oxidized to Fe³⁺. Bivalent Fe is easily oxidized to trivalent by atmospheric oxygen if it is in form of hydroxide Fe(OH)₂. This substance can be received from Fe (II) sulphate when affecting it by alkaline solution or ammonium hydroxide solution.

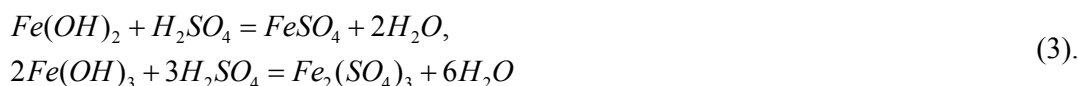


Fe (II) hydroxide is contained in aqueous solution in the form of small laminas. To oxidize Fe²⁺ to Fe³⁺ it is enough to pass it through air suspension, during this the below reaction will take place:

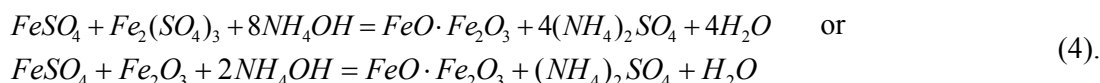


Fe(OH)₃ ginger sediment is formed, in particular Fe (III) oxide crystalline hydrate Fe₂O₃ · nH₂O.

Having received by this way the mixture of Fe (II) hydroxide and Fe (III) hydroxide, the reverse reaction of neutralization by sulphate acid can be carried out and the result will be the formation of Fe sulphate in the needed proportion $Fe^{3+}/Fe_{3ae}=2/3$:



The last stage of the synthesis can be, according to the chemical characteristics of the substances, the reaction of the received mixture of Fe sulphates with ammonium hydroxide, in case of its excess, with magnetite formation, which can be described by such reaction equation:



Under the air influence bivalent Fe is oxidized to trivalent, the substances of which are hardly resoluble, and it settles on the surface of magnetite particles. This characteristic will contribute to more deep reaction and sediment production, which will easily separate from the reaction solution.

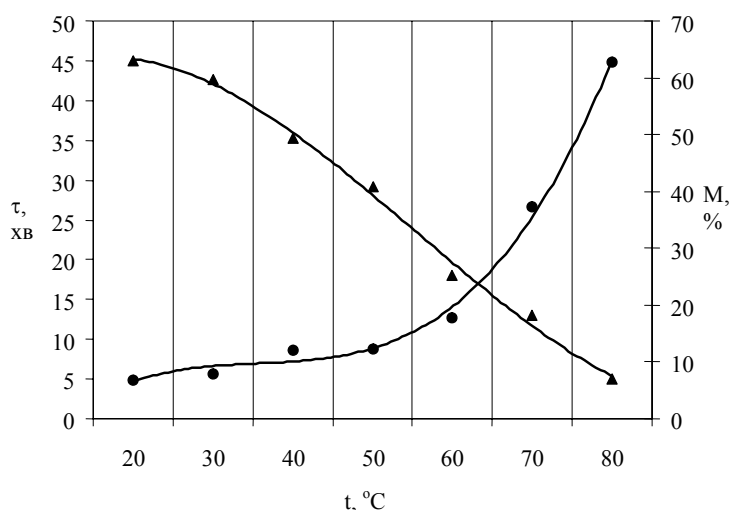


Figure 4. The dependence of transformation time and ammonia loss from the reaction mixture temperature.

The first stage of the synthesis process is the performing of a chemical transformation according to the reaction (1). But it is urgent to keep in mind that the wastes contain the excess quantity of sulphate acid, the neutralization of which requires additional quantity of alkaline solution.



To determine the optimal temperature of the synthesis first stage the experimental research was conducted, which studied the temperature influence on the time of the reaction carrying out and ammonia inputs from the reaction solution. The quantity of spent ammonia was calculated by the excess of hydroxide ammonium, which was added to the solution to finish the reaction. The results of the experimental research is presented in the graphic dependences on Figure 4.

Having analyzed the received dependences we can conclude that after the reaction mixture temperature becomes higher than 60 °C the sharp increase of ammonia loss from the solution takes place. So all the transformations should take place within the temperature of 50÷60 °C. In this case the duration of the process will be 20 minutes, which can be seen from the dependences. The reaction mixture warming up is performed due to the heat from exothermic reaction of neutralization, and the heat from external heat carriers.

After the completion of the first stage of synthesis process the reaction mixture temperature is 50÷60°C. The oxidation process which takes place in the same reactor is also carried out in established temperature conditions. Then it is important to define the optimal promptness of the mixer and the approximate time of oxidation process duration under these conditions.

To determine the oxidation process dependence from the regime parameters, the experiments were carried out with the different air inputs and speeds of the mixer device. The data analysis showed that the transformation level increases dramatically with the increasing the mixer speed to 100 turns/min, and then it stays unchangeable. This indicates the limiting stage move from outer diffusive area till inner diffusive. In the conditions of air input 0.4 l/sec on 1 kg $FeSO_4$ there still remains the needed transformation stage. The determined data can be used as guiding line for iron vitriol production technology development.

On the base of the experimental research the technology of iron vitriol recycling with the $FeO * Fe_2O_3$ receiving was developed.

The production of yellow ferrioxide pigment

The task that lays in the basics of the technology is to improve the color characteristics of yellow ferrioxide pigment by the way of creating more favorable conditions for the synthesis of incipient particles and elimination of the stage of metallic iron preparing and use during the synthesis. This allows to simplify the technological process and to improve the quality of the end product, and also to reduce the synthesis time.

This goal can be achieved when inserting the following stages to the technological structure chart:

- dissolving the titanium(IV) oxide production waste in a water;
- removing of cations of titanium, aluminium, manganese and colloidal and insoluble parts;
- solution acidation;
- receiving of colorant suspension embryo;
- interaction of the received suspension embryo with sulphuric acid until pH=2,0-2,5;
- keep with this pH value for 15-30 minutes with the temperature 20-50°C;
- mixing the received suspension embryo with subacid Fe (II) sulphate solution;
- receiving of the colorant suspension.

The use of the improved technology of yellow ferrioxide pigment production allows to:

- ◆ increase Fe (II) sulphate utilization;
- ◆ create favorable conditions for crystalline pigment particles growth;
- ◆ stabilize the color characteristics of the end product;
- ◆ simplify the technological process because of eliminating the stages of metallic iron preparation and use;
- ◆ shorten the synthesis time by a factor of 1,5-2;
- ◆ shorten the energy use time by a factor of 1,5-2;

CONCLUSIONS

The complex strategy of Fe (II) sulphate (which appears to be a waste of titanium (IV) oxide production) utilization by the way of introducing large-tonnage production was developed, which allows to avoid completely the ecological risk from the waste impact on the environment.

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