

Technological analysis of liquid waste parameters in treatment system for phosphorus production

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Abstract. This study considers the problem of analyzing a complex hierarchical system of phosphorus production wastewater treatment, which is characterized by considering the process of sedimentation of elemental phosphorus sludge particles and mechanical impurities. The study presents a framework for decision-making on the purification of wastewater from phosphorus production, which is contaminated with toxic impurities and must meet sanitary norms. The framework considers the reagents introduced, as well as the increased mineralization of water, which cannot be discharged into the water body for ecological reasons. Instead, it is reused in production. It is demonstrated that for mechanical treatment of sewage from elemental phosphorus and suspended solids, as well as to improve sedimentation of particles, iron sulphate is used as a coagulant. The action of this coagulant is similar to that of sulphuric acid aluminum, which is widely used for water treatment. Thus, a complex engineering approach is presented for a complex system of phosphorus production wastewater treatment.

1 Introduction

The complex hierarchical system of yellow phosphorus production generates process effluents in the amount of 4-5 m³ per 1 ton of phosphorus. These effluents are contaminated with phosphorus and other toxic impurities, the purification of which to sanitary standards is a very difficult scientific, technical, and expensive practical task [1-2]. Even if the purification, process were to be carried out, the impurities present in the wastewater and reagents introduced in excess would result in highly mineralized water, which could not be discharged into water bodies or used in production without repeated dilution [3]. Consequently, all phosphorus production facilities in China and Kazakhstan employ a simplified scheme for treating phosphorus-containing effluents to standards that allow their use in technological processes in closed cycles and irretrievably.

The technology of such a scheme is as follows. The effluent is subjected to primary sedimentation using a coagulant, whereby the main mass of elemental phosphorus and

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mechanical impurities are precipitated in the form of sludge. This sludge is then burned together with sludge from the sedimentation of raw phosphorus to obtain phosphoric acid. The clarification of wastewater is achieved through the neutralization of the wastewater with milk of lime [4]. This process results in the formation of insoluble salts of calcium phosphates and fluorides, as well as insoluble hydroxides of silicon and some metals [5]. The obtained suspension is subjected to secondary sedimentation with the use of a flocculant. In addition to the sludge formed during the neutralization process, the bulk of elemental phosphorus that passed through the primary sedimentation tank is also precipitated [6, 7]. The sludge, following additional compaction, is then subjected to burial in the sludge collector. The clarified water is collected in two storage tanks, from which it is supplied for reuse as needed. One of the storage tanks is capable of being heated with superheated steam. The initial data are based on the experience of operating industrial systems of phosphorus-containing wastewater treatment and reuse [8].

2 Materials and methods

A feasibility study was conducted to assess the recommended method and to determine the optimal capacity of the wastewater treatment system. Four variants of phosphorus production from different raw materials at an acidity modulus of 1 were considered, as shown in Table 1.

Table 1. Technological parameters for different types of sinter and pelletized materials.

Technological parameters	Agglomerate from raw ore		Concentrate sinter Furnace No. 1	Concentrate pellets Furnace No. 2
	Furnace No. 1	Furnace No. 2		
Phosphorus capacity, tons/year	13500	27000	25600	24900
Phosphorus capacity, t/day (average)	44.88	89.76	85.2	82.8
Phosphorus capacity, tons/day (maximum)	64.08	126.16	12168	118.32
Phosphorus losses with wastewater, kg/m ³	2.6	2.6	2.63	2.6

The capacity of the system was selected based on the considered variants, with the objective of treating the normalized amount of wastewater from two furnaces. This decision was informed by the results of the surveys [9]. When selecting the size of settling tanks and other equipment, the possibility of operation of furnaces and the corresponding consumption of water effluents at maximum capacity (130 t/day) was considered.

The following reagents are required for the wastewater treatment system burnt lime (440 tons per year in terms of 100% CaO), iron sulphate (75 t/year), and polyacrylamide (1.25 tons per year in terms of 100% of the substance according to the relevant standards). Expenditures of reagents, energy resources, and other materials are similar to the regulatory scheme operating in our country [10].

The complex hierarchical treatment system receives effluents in the following quantities per day: from phosphorus condensation (double the volume displaced by phosphorus is accepted) – 108; from phosphorus storage – 54; from pipelines washing – 108; from railway tank station – 54; from hydraulic gates – 15; from sludge incineration department – 25; from laboratory and floor flushing department – 34. The composition of the effluents is presented in Table 2.

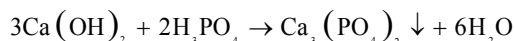
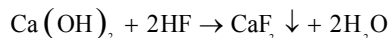
Table 2. Wastewater composition before treatment and by stages of treatment.

Impurity	Impurity content, mg/l		
	Incoming for treatment	After settling tank No. 1	After settling tank No. 1
pH	2.0 – 6.5	2.0 – 6.5	6.5 – 7.5
P ₄	600	100	10
suspension of substances	1000	200	100
F	300	300	50
P ₂ O ₅	3000	3000	500
SiO ₂	100	100	10
SO ₄ ²⁻	50	200	200
Cl ⁻	150	150	150
CN ⁻	50	10	10
Fe	30	100	10
Ca ²⁺	60	60	100
Mg ²⁺	50	50	30
K ⁺ + Na ⁺	100	100	100

The initial stage of the system entails mechanical treatment of the effluent derived from elemental phosphorus and suspended solids [11]. Coagulants are typically employed to enhance sedimentation of particles. Iron sulphate is recommended as a coagulant, the action of which is analogous to aluminum sulphate, which is widely utilized for water treatment. In addition to the coagulating action, iron ions also exhibit binding properties with respect to toxic and volatile substances, particularly at a pH of 6.5, where cyanide ions form complex ions with them. This reaction is represented by the equation $\text{Fe}^{++} + \text{HCN}^- \rightarrow [\text{Fe}(\text{CN})_6]^{4-}$.

The formation of complex ions results in a reduction in toxicity, volatility, and the potential for the formation of insoluble compounds with ions of numerous metals. This process eliminates the possibility of cyanide accumulation in wastewater to dangerous concentrations when reusing treated wastewater.

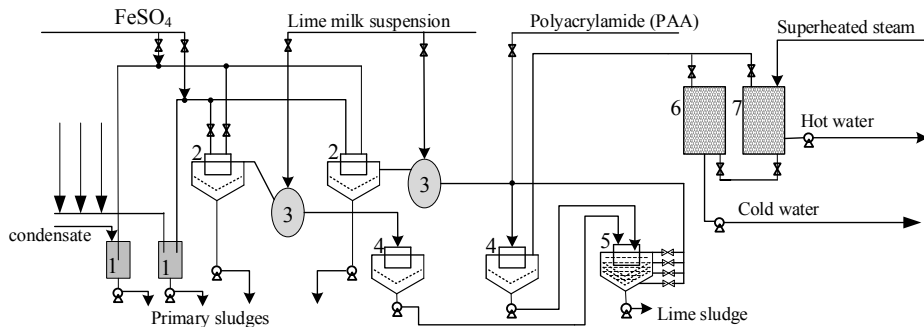
The optimal specific consumption of iron sulphate is 10 mg FeSO₄·7H₂O per 1 mg CN⁻, or alternatively, at a CN⁻ concentration of 50 mg/l, the daily consumption is 394 m³/day. The quantity of iron sulphate required is 297 kg, which is approximately equivalent to 19 m³ of a 1% solution, or 50 l/m³ of wastewater, or 0.5 kg/m³ FeSO₄·7H₂O. The specific flow rate of the analog, Al₂(SO₄)₃·18H₂O, is typically 0.36 to 0.6 kg/m³. Both sediments are amorphous and friable. The wastewater clarified in the first settling tank is neutralized to pH=6.5. Milk of lime is recommended as a neutralizing agent. In contrast to other neutralizing reagents, such as caustic soda, soda ash, and others, milk of lime, in conjunction with acidity removal, forms insoluble calcium compounds with basic impurities, precipitated in the second settling tank:



In conjunction with neutralization, wastewater is demineralized and treated for phosphorus. The specific consumption of milk of lime is recommended to be 3 kg/m³ of effluent in terms of CaO. This equates to 31m³ of 4% milk of lime per day or 75-80 l/m³ of effluent. The selection of this concentration is supported by empirical evidence, as the

concentration of milk of lime of 10%, which is typically included in projects, is observed in practice at various plants for various reasons [12]. The clarification of the neutralized slurry in the second settling tank is conducted using flocculants. Polyacrylamide (PAA) and its foreign analogs have been demonstrated to be effective flocculants. It is recommended that the specific consumption of PAA be 5 mg/l in terms of 100% substance. After the addition of the coagulant solution and lime milk suspension, the daily consumption of PAA will be 2.2 kg, or approximately 5 m³ of its 0.05% solution, at a dosage of 11-12 l/m³ of effluent. The treated wastewater, the composition of which is presented in Table 2, is heated by superheated steam to 80–90°C if necessary and is used repeatedly. The quantities of wastewater used per day are as follows: for the protective layer in storage tanks, 54 m³; for washing of pipelines, 108 m³; for washing of railway tanks, 54 m³; and for preparation of bark milk, 38 m³. Furthermore, without heating, it is irretrievably used for quenching or granulation of fire-liquid slag from the calculation of phosphorus production (90 t/day), the formation of slag (at least 900 t/day), and specific water consumption (0.55 m³/t of slag) – 495 m³, 31 m³ with sludge from pumps.

Consequently, the total effluent volume, including the input water with reagents, is 449 m³/day, with a flow rate of 780 m³/day. The additional balance is 331 m³/day, indicating that the effluent can be fully reused. Figure 1 illustrates the principal scheme of the phosphorus-containing effluent treatment system.



1 - averaging tanks, 2 - primary settling tanks, 3 - neutralizers, 4 - secondary settling tanks, 5 - lime sludge compactor, 6 - cold treated water storage tank, 7 - hot treated water storage tank

Fig. 1. Principle scheme of phosphorus-containing wastewater treatment system.

It is recommended that effluents from phosphorus condensation, storage, and pipeline flushing, as well as from the railroad tank car station and phosphorus sludge incineration plant, be delivered after phosphorus traps. This will help to reduce phosphorus losses and shorten the distance of phosphorus pumping from the traps [13]. It is also recommended that the traps be installed near possible sources of phosphorus emissions with runoff and that they be maintained and emptied in a timely manner by personnel working in these areas.

Since settling tanks and neutralizers operate in an optimal mode only at a uniform load and with a relatively constant composition, the effluent enters the averaging tanks. In a short time, the largest inflow of effluent (which may be one-time) can be at flushing of pipelines and displacement of the protective water layer during phosphorus pumping. It is therefore recommended that at least 130 m³ of volume be allocated to the averaging tanks, situated at a depth of 0.5-0.7 m from the bottom. Despite the sewage intake being located at the bottom, experience has shown that at the bottom of the averaging tanks sludge accumulates to the point of clogging the pump intake. Consequently, it is recommended

that a cone-shaped bottom be constructed for the averaging tank, equipped with a device for periodic heating and pumping of sludge.

From the averaging tanks, the effluent is continuously pumped by submersible pumps with a uniform load to the central cups of the primary sedimentation tanks. To ensure the further flow of effluent by gravity to the secondary settling tanks, the settling tanks and other equipment should be placed at an appropriate height. At a sludge settling rate of 0.2 m/h and an average hourly load of 16.4 m³/h, the required clarification surface is 107 m². Furthermore, at an average hourly load of 16.4 m³/h and a maximum load of 23.4 m³/h, the diameter of the settling tank should be at least 12 m. The bottom of the tank should be conical with an angle of inclination of at least 30 degrees, equipped with a scraper mechanism, heated by blind steam, and equipped with a discharge device for sludge.

The iron sulphate is dosed into the effluent in the pipeline at 6-7 m before its flow into the sedimentation tank. The neutralization process is conducted for a minimum of 40 min. The neutralized slurry is then directed to the central cups of the secondary sedimentation tanks (4). This is done at no less than 6-7 m from the tumbler in the pipeline (or trough) in the suspension, where a polyacrylamide solution is dosed. The dimensions and discharge device for sludge in the secondary sedimentation tank are identical to those of the primary sedimentation tank, with the exception of the absence of heating of the conical bottom.

Treated water is directed to storage tanks 6 and 7. Alternatively, it may be directed to either tank, depending on the level of the second tank. If the second tank is filled, the water is sent for reuse. Based on the daily supply, the volume of the storage tanks is recommended to be 200 m³ each. One of the tanks, positioned at scheme 7, is equipped with a superheated steam supply for water heating.

3 Results and Discussion

The quantity of solid waste and its composition are as follows: sludge from primary sedimentation tanks, 6 m³/day, specific gravity 1.1, solid/liquid ratio of 1/10, total phosphorus content of 3% or 198 kg/day. The solid mineral content is 402 kg/day, with a variable composition including silicates, aluminosilicates, calcium fluorides and phosphates, soot and its compounds, and iron compounds. The sludge from the secondary sedimentation tanks has a specific gravity of 1.02 and a solid/liquid ratio of 1/10 after compaction. It contains 1.15 % total phosphorus, or 38 kg/day. The solid mineral content is 193 kg/day, and its composition is variable, including sulphate phosphates, calcium fluorides, magnesium, iron, and silicon hydroxides. Sludge from averaging tanks is collected on a periodic basis, approximately once every two weeks, and accounts for 10 to 15 m³. This sludge is subsequently incorporated into the sludge from the primary sedimentation tanks. A shortage of lime is observed, with a daily deficit of up to one ton. In order to operate in the sludge sealing mode, it is recommended that pipes with gate valves (see Fig. 1) be cut along the cylindrical part of the sealer 5 in 25-30 cm. Prior to pumping and pumping out the sludge, it is necessary to release the accumulated water by directing it, starting from the upper one, into the accumulators through the aforementioned pipe. The observation is conducted visually, and thus each pipe should be equipped with a sampler, as the glass windows will become cloudy over time.

4 Conclusion

It has been demonstrated that when working with sinter and phosphorus-containing effluents with a neutral or even alkaline reaction, condensation may result in the formation of such effluents. Furthermore, the necessity to have reserve equipment for the time of

settling tanks shutdown, for repair or desliming, has led to the recommendation that three technological strings be installed. In the event that neutral or alkaline effluents are formed in the phosphorus condensation system, they are separated from the general flow and directed through a separate line. After clarification, they are discharged into the cold water storage 6, which is used for slag quenching. This storage area is safe for the use of alkaline water. At the neutralization station, settling tanks and all other containers with phosphorus-containing effluent are covered. Waste gases are fed by a fan to a scrubber irrigated with milk of lime for purification. Given the experience of the neutralization plant's functioning and the absence of comments on this position, it is recommended that the design consider the number of gases proportional to the number of units of the sheltered equipment. For scrubber irrigation, it is necessary to use lime milk from the general collection.

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References

1. S.V. Pancnekhko, M.I. Dli, A.A. Bykov, Simulation and algorithmization of analysis of heat and mass transfer processes in chemical electrothermy units in non-ferrous metallurgy in *Non-Ferrous Metals*, **52-1**, 46-54 (2022)
2. V.P. Meshalkin, T.A. Vagramyan, D.V. Mazurova [et al.], Development of a Power-and-Resource-Saving Combined Low-Temperature Chemical Engineering Process of Crystalline Phosphatizing in *Doklady Chemistry*, **490-1**, 19–21 (2020)
3. B.M. Smailov, B.S. Zakirov, O.K. Beisenbayev, Thermodynamic-kinetic research and mathematical planning on the obtaining of phosphorus-containing components based on cottrel dust from phosphorus production waste in *Rasayan Journal of Chemistry*, **15-04**, 2274-2279 (2022)
4. M. Boscolo, E. Padoano, L. Parussini, CFD Analysis of Low-Cost Solutions to Minimize Gas and Dust Emissions during the Emergency Opening of Blast Furnace Bleeders in *Applied Sciences*, Switzerland, **12-5** (2022)
5. V.P. Meshalkin, N.S. Shulaev, V.V. Pryanichnikova, Theoretical Bases of Electrochemical Cleaning of Oil-contaminated Soil in IV Congress "Fundamental Research and Applied Developing of Recycling and Utilization Processes of Technogenic Formations", Yekaterinburg: Knowledge E Engaging minds, 425–431 (2020)
6. V.A. Kukartsev, V.V. Kukartsev, V.V. Tynchenko, The Technology of Using Liquid Glass Mixture Waste for Reducing the Harmful Environmental Impact in *Materials*, **15-3** (2022)
7. R. Bai, Sh. Wang, X. Kong, Magnetized vermiculite loaded with waste polishing powder to recover phosphorus in waste water in *Journal of Water Process Engineering*, **49**, 103094 (2022)
8. V. Orekhov, V. Bobkov, E. Morgunova, Features of the method for solving the inverse problem for determining the heat capacity and thermal conductivity of phosphate ore raw materials in *AIP Conference Proceedings*, **2999(1)**, 020055 (2023)

9. Ju. Suer, F. Ahrenhold, M. Traverso, Carbon Footprint and Energy Transformation Analysis of Steel Produced via a Direct Reduction Plant with an Integrated Electric Melting Unit in *Journal of Sustainable Metallurgy*, **8-4**, 1532-1545 (2022)
10. J. Li, H. An, W. Liu, A. Yang, M. Chu, Effect of basicity on metallurgical properties of magnesium fluxed pellets in *Journal of Iron and Steel Research International*, **27-3**, 239-247 (2020)
11. F.O. Unuofin, M. Siswana, Enhancing organic waste decomposition with addition of phosphorus and calcium through different sources in *International Journal of Recycling of Organic Waste in Agriculture*, **8-2**, 139-150 (2019)
12. B. Ismailov, B. Zakirov, A. Kadirbayeva, Methods for Obtaining Phosphorus-Containing Fertilizers Based on Industrial Waste in *Inorganics*, **11-6**, 224 (2023)
13. F. Sevim, H. Sarac, M.M. Kocakerim, A. Yartaşı, Dissolution kinetics of phosphate ore in H_2SO_4 solutions in *Industrial and Engineering Chemistry Research*, **42-10**, 2052-2057 (2003)