Water cycle optimization for complex fertilizer manufacturing based on quality improvement of waste water treatment

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Abstract

The necessary precondition of transition to reserved water circulating systems in the mineral fertilizers plants is the increase of the waste water purification degree. In this connection, in the present work the results of researches of thin purification of waste water on the base of a carbone method are discussed. As a result of study of the process various variants realization has been established, that the deepest purification degree is achieved at its realization on base of two stage scheme of the basic purification without preliminary branch of a deposit before carbonization. The practical realization of the developed method of waste water purification will ensure an opportunity of stable functioning of reserved water circulating systems in manufacture of fertilizers and will allow to prevent 'the fluoration' of others water circulating systems.

Аннотация

Необходимой предпосылкой перехода на замкнутые водооборотные системы в производстве минеральных удобрений является повышение степени очистки сточных вод. В результате изучения различных вариантов осуществления процесса установлено, что наиболее глубокая очистка достигается при ее проведении на базе двухстадийной схемы основной очистки без предварительного отделения осадка перед карбонизацией. Результаты заводских испытаний подтвердили данные лабораторных исследований. В частности при начальном содержании фтора в сточных водах в ходе испытаний от 3011 до 7920 мг/л, остаточное содержание фтора колебалось от 0,22 до 0,6 мг/л (по сравнению с 20-25 мг/л по действующей схеме). Практическая реализация разработанного метода очистки сточных вод обеспечит возможность стабильного функционирования замкнутых водооборотных циклов в производстве фосфорных удобрений и позволит предотвратить «зафторивание» других водооборотных циклов.

Keywords: Water cycle optimization; fluorine and phosphorus; waste water; reagent method; neutralization.

Introduction

Due to the recent aggravating ecological situation, all the countries have toughened their environmental legislation and the related requirements imposed on industrial enterprises. Fluorinated and phosphorus-containing waste water is one of the most large-tonnage waste produced by complex fertilizer enterprises. Therefore, one of the major challenges in the field of environmental protection facing the industry is the change-over to closed water use system based on zero waste discharge from industrial sites by its technological recirculation and fresh water use

only to compensate the imbalance resulting from water leakage with final products and partly water losses.

Organization of several autonomous water cycles is the basic concept of zero-discharge water systems. The key factor for the organization of such cycles is the uniformity of the qualitative composition of water used in particular industry or group of industries and the produced waste water. Thus, the most contaminated fluorinated and phosphorus-containing waste water in the complex fertilizer manufacturing is allocated in the form of «fluoric» water cycle.

As it is seen from the scheme, «fluoric» water cycle contains the stage of intermediate treatment of waste water at the neutralization station. Moreover, one of the advantages of closed water cycles is that you don't need to purify the waste water to MPC values but only to the values of ionic and heterogeneous impurity concentrations, thus allowing this water to be reused in the technological process.

The system of closed water cycles is implemented in almost all industrial enterprises (Figure 1).

However, the analysis of existing water cycles and survey results of neutralization station activity of some enterprises revealed that the forming of schemes of water cycles and cleaning regime is organized without special considerations to waste water qualitative and quantitative composition of different workshops as well as physical-chemical and kinematic patterns of neutralization process in $CaO-H_3PO_4-H_2SiF_6-H_2O$ system in the field of dilute solutions under imbalanced conditions. Qualitative and quantitative composition of waste water discharged to waste water treatment plant was not often to meet the regulatory requirements and the remaining content of impurities in clarified water exceeded the specified values. Thus, the survey of one enterprise revealed that the content of airborne dusts in clarified water after neutralization reached 7,000 mg/l (standard value being max 200 mg/l), fluorine to 150 mg/l, phosphorus from 50 to 600 mg/l (standard value being max 50 mg/l). As a result, it proved to be impossible to allocate a separate «fluoric» water cycle, to rapidly fill slurry reservoirs and to clean them, resulting in contamination of pure water cycles that had a negative impact on the operation of all facilities, in particular, heat-exchange equipment.
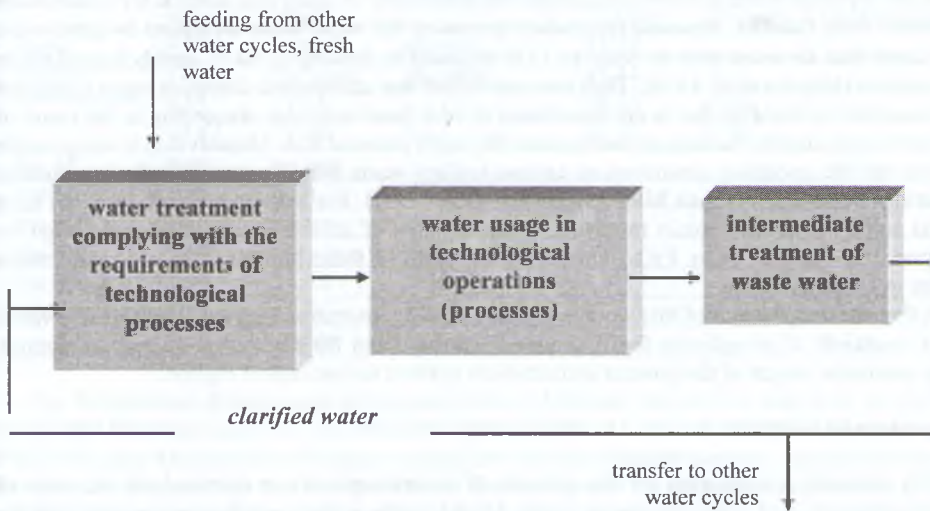
feeding from other
water cycles, fresh
water

| water treatment complying with the requirements of technological processes | water usage in technological operations (processes) | intermediate treatment of waste water |

clarified water

transfer to other
water cycles

Figure 1 The principal scheme of closed water cycles organization

But even in case of allocation of «fluoric» water cycle as a separate cycle recycling is not always possible. So, if the water balance of «fluoric» water cycle is negative and the volume of generated waste water is less than or equal to the volume of water injected into the cycle, recycling proves to be feasible. As shown by the surveys, when some enterprises organize «fluoric» water cycle they have positive imbalance in which part of clarified water is surcharged and should be transferred to other water cycles or discharged into water reservoirs. But in this case there occur serious problems because the content of fluoride ions in water of other water cycles does not exceed the MPC values and additional fluorination is unacceptable (Lamp *et al.* 1979).

Thus, fine or integrated waste water treatment to reach the residual concentrations not exceeding the MPC remains relevant to the water cycle optimization problem.

Reagent method at the neutralization stations is limited in use. This is explained by the fact that in the process of waste water reagent treatment the fluorine contained in waste water in the form of hexafluorosilicic acid binds to calcium ions and precipitates in the form of calcium fluoride. Although the solubility of calcium fluoride is negligible, it corresponds to residual value of fluoride ion in 16 mg/l water (when MPC=0.75). Under real conditions with other present ionic impurities the residual value of fluorine comes to 30-50 mg/l.

The most promising methods are combined methods which include main treatment stage, in which the content of impurities is reduced to several tens of milligrams per liter and tertiary treatment stage. It is proposed to use traditional lime method in the first stage and sorption, electrochemical and ion-exchange methods for tertiary treatment. These methods provide almost complete removal of impurities but their usage for waste water treatment of large industrial enterprises is limited by some reasons, first of all by economic ones. At present one of the most advanced methods is a carbon method. The principle of this method is that the excess of lime milk is injected in water, this water is treated by carbon dioxide and then calcium carbonate is formed with the ionic impurities being adsorbed on its crystals. Known as a reagent method of fractional precipitation, this method is used for extracting and concentrating of trace elements from seawaters (Khozhainov *et al.* 2000).

In the literature there is information about the possibility of using this method for waste water treatment from fluorine. Japanese researchers proposed the waste water treatment by lime to the pH values that are more than or equal to 11.0 followed by heating to 60 °C and polyacrylamide coagulation (Miyake *et al.* 1978). Then the suspension was carbonized. Clarified water contained to 25 mg/dm^3 of fluorine that is not considered to be a good indicator. According to the result of research conducted by Russian scientists under the supervision of B.A. Dmitrevskiy it was possible to find out the operating conditions of carbon tertiary waste water treatment reducing fluorine impurities to values less than MPC (Saibatalov *et al.* 1987). For this experiment scientists used model solutions which contain relatively small amounts of ionic impurities: 60 - 365 mg/l by fluorine, 800-1,650 mg/l by P_2O_5. Though, the content of these impurities in real waste water comes to 10 g/l and more.

In that context, the aim of this work is to study the effectiveness of various types of fine waste water treatment of phosphorus fertilizer manufacturing from fluorine based on carbon method, study particular stages of the process and establish optimal technological regime.

Materials and methods

This research is conducted on the samples of model waste water prepared on the basis of hexafluorosilicic and orthophosphoric acids. Model waste water content corresponds with the

content of real waste water of one industrial enterprise: 2.87-10.4 mg/l of fluorine-ion, 6.4-10.0 mg/l of phosphorus expressed as P_2O_5.

There are some different variants of the technological process have been studied:

⇒ the 1st variant – carbonization of clarified waste water after the main treatment stage without additional injection of lime milk;

⇒ the 2nd variant – carbonization of neutralized suspension after the main treatment stage without additional injection of lime milk;

⇒ the 3rd variant – carbonization of clarified waste water after the main treatment stage with additional injection of lime milk in waste water.

Results and discussion

The research results of treatment variants named above are shown in Table 1. According to the analysis results the traditional reagent method of treatment using lime milk doesn't provide high degree of treatment. Moreover, increase of injected calcium hygroxide at high pH values leads to negative effect – fluorine content increases from 33,72 mg/l when pH=9,75 to 43,33 mg/l when pH=11,9. This fact correlates with the earlier findings about solubility rise of calcium fluoride with pH rise over 10-11 (Dormeshkin et al. 2004). At the same time two-stage treatment processing helps to improve its efficiency, but nevertheless the residual fluorine content is significantly higher than MPC values.

Comparison of different variants of carbon tertiary treatment leads to the conclusion that the highest degree of treatment is achieved by the 3rd variant of technological processing.

Table 1 Comparison of various types of waste water treatment from fluorine
(Content in the source water, mg/l: F – 3600; P_2O_5 – 9860.)

Method of treatment	pH of neutralization		pH of carbonization	Fluorine content, mg/l		
	the 1st stage	the 2nd stage		after the 1st stage	after the 2nd stage	after carbonization
Basic	9.75	no test	no test	33.72		
(without	11.90	the same	the same	43.44		
carbonization)	9.55	11.45	- « -	29.30	11.40	
	10.47	12.05	- « -	41.50	8.30	
the 1st	9.00	no test	7.75			30.11
variant	5.50	9.50	8.00			30.00
the 2nd	10.05	no test	6.00			32.26
variant	9.50	the same	8.00			30.91
the 3rd	8.05	11.95	8.46			2.44
variant	8.81	12.36	8.14			0.75
	9.90	12.80	7.76			0.71

The fundamental difference of this variant is the additional injection of lime milk in clarified water after the main treatment just before the carbonization. As the carbon method of treatment is based on cation and anion liquid-phase adsorption onto the collector surface – nascent precipitate of calcium carbonate –the availability of active CaO in liquid is the necessary precondition for this method. So it is assumed that the low efficiency of carbon treatment by the first two variants results

from the inadequate availability of active CaO. To confirm this hypothesis it was studied the relationship between the active CaO content in liquid and pH of neutralization value.

Table 2 Relationship between the CaO_{act} content in liquid, CO_2 consumption and pH of neutralization value
(Content in the source water, mg/l: F – 2870; P_2O_5 – 10000.)

pH of neutralization	CaO_{act} content, %	CO_2 consumption for carbonization to pH 8,0, kg/m³ of water
9.50	none	0.010
10.00	0.006	0.050
10.70	0.07	0.130
11.64	0.022	0.173
11.85	0.031	0.240
12.00	0.042	0.330

As it is seen from the Table 2, there is no $CaO_{act.}$ in liquid over the pH range to 9,5. This is the explanation of no solid phase in the carbonization process of waste water with pH lower than 10 as well as the residual fluorine content fall-off following the additional injection of lime milk after the main treatment stage. Accordingly to this the necessity of the additional injection of lime milk before the carbonization is confirmed.

Moreover, it was established from the additional studies, that phosphorus and fluorine content changes in the source waste water has no appreciable impact on active CaO content in liquid when pH values of neutralization are equaled.

These findings correlate well with the research results of the effect of pH of neutralization on the residual fluorine content (when pH of carbonization is constant and equal to 7,0).

Table 3 The effect of pH of neutralization on the residual fluorine content
(pH of carbonization is equal to 7,0)

pH of neutralization	9.70	10.70	11.70	12.50	12.90
Residual fluorine content, mg/l	12.67	7.80	3.18	1.00	0.79

Apart from pH of neutralization the important technological characteristic which determines both the efficiency of treatment and chemical-engineering properties of produced precipitates is pH value of carbonization.

The research results of the effect of pH of carbonization on the degree of treatment (residual fluorine content) and chemical-engineering properties of produced precipitates are shown in the Table 4.

Table 4 The effect of pH of carbonization on the residual fluorine content in liquid and suspension properties

pH of carbonization	9.80	9.00	8.50	8.00	7.50	7.00	6.50	6.00
The fluorine content in the filtrate, mg/l	2.08	1.52	0.50	0.48	0.43	0.48	0.57	0.75
Clarification speed, m/h	2.41	1.97	1.91	1.59	1.39	1.46	1.52	1.56
Filtration coefficient, cm/s*10^{-5}	7.62	7.60	7.52	7.13	6.11	6.02	6.00	no test
Final volume of sludge sediment (% of the volume of initial suspension)	24.10	23.08	20.00	18.80	21.90	26.15	28.5	the same

As it is seen from this Table, the minimum residual fluorine content is equal to the pH range from 6,5 to 8,5. However, the carbonated suspension properties and chemical-engineering properties of produced precipitate go down when pH is lower than 8,0. That is why the optimum pH value of carbonization is 8,0-8,5. It is known from the literature that to achieve high degree of impurity coprecipitation, the building-up and precipitation process of collector (in this case – calcium carbonate) should be carried out when pH values close to pI value (Saibatalov *et al.* 1987). With that the precipitate of calcium carbonate with feebly marked crystallinity is formed on the surface of which impurity coprecipitation is happen. Value of pI for $CaCO_3$ is equal to 8,6 and close to optimum pH values of carbonization established by experiment.

As mentioned earlier when traditional reagent methods are used the achievable depth of waste water treatment is determined by the solubility product value of produced poorly soluble compounds. But previous researches showed that it is possible to achieve higher degree of waste water treatment from the main ionic impurities under certain conditions of technological process (Dormeshkin *et al.* 1987). In particular it was established that the main quantity of fluorine and phosphorus goes into solid phase when pH values are equal to 5,0-5,5. Moreover, the sludges determined at these pH values contain P_2O_5 to 25-28 % and it is close to phosphorus content in conditioned phosphate feedstock. After intermediate separation of solid phase on the second stage when pH is equal to 5,0-5,5 the residual content of fluoride ions and PO_4^{3-} in liquid is not large and it provides the achievement of higher degree of treatment in comparison with traditional one-stage scheme.

That is why it can be assumed that the organization of fine carbon tertiary treatment based on two-stage scheme of main treatment mentioned above will provide more effective reduction of residual content of fluoride-ion.

The obtained results confirmed those suspicions (Table 5).

Table 5 Research results of fine carbon tertiary treatment based on two-stage scheme of main treatment

Main treatment				Fine tertiary treatment			
the 1st stage		the 2nd stage		with the preliminary sediment detachment		without the preliminary sediment detachment	
pH	Fluorine content, mg/l	pH	Fluorine content, mg/l	pH of carboni-zation	Fluorine content, mg/l	pH of carboni zation.	Fluorine content, mg/l
5.8	13.41	10.55	2.08	7.0	0.42	7.0	0.20
5.5	16.50	9.80	4.15	7.0	0.50	7.0	0.24

The residual fluorine content ranged from 0,2 to 0,5 mg/l that was lower than in other variants of carbon tertiary treatment. The best results of treatment were achieved by carbonization of unfiltered suspension after the second stage of neutralization. This fact has positive practical value because it helps to simplify the technological scheme by elimination of thickening and suspension filtration stages.

The laboratory findings are completely confirmed by the results of industrial tests on Gomel chemical plant. In particular, if the initial fluorine content in waste water during the tests was from 3011 to 7920 mg/l, then the residual fluorine content ranged from 0,22 to 0,6 mg/l (in comparison with 20-25 mg/l under the current scheme).

Conclusions

So there are some conclusions based on given results:

• One of the main technological parameters which determine the fine carbon treatment is the quantity of lime milk injection and pH value.

• The minimum content of fluoride-ions complies with the pH value equaled to 7,0-8,5. However, the main chemical-engineering properties of produced precipitate go down when pH is lower than 8,0. That is why the recommended pH value of carbonization is 8,0-8,5.

• Comparison of different variants of technological process leads to the conclusion that the most integrated waste water treatment from the fluorine is achieved by before carbonization. In this case the residual fluorine content is 0,2-0,5 mg/l.

• The implementation of recommendations for changes in waste water forming scheme with consideration of special aspects of their qualitative-quantitative content, regime of their neutralization, necessity of maintaining the optimal pH values and providing with necessary time of neutralization allowed to achieve the significant reduction of impurity content to regulated values without considerable additional costs, and the implementation of combined scheme of stage waste water treatment with following carbon tertiary treatment helps to provide the reduction of fluorine content from 0,22 to 0,6 mg/l (in comparison with 20-25 mg/l under the current scheme). Practical using of developed method of fine fluorinated waste water treatment will make it possible to stable function the closed «fluoric» water cycle for phosphorus fertilizer manufacturing and optimize the organization of all water cycles of enterprise.

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