

IMPROVEMENT OF THE PHOSPHORIC ACID CONCENTRATING PROCESS IN THE PRESENCE OF SURFACTANTS

Bronislava Kopyleva, Dr. of Science
New York

This paper will discuss proposed method of concentrating phosphoric acid in the presence of surfactants. This method makes possible to reduce energy costs during evaporation with a simultaneous reduction the fluorine concentration up to 0.2-0.3% in the acid containing 52-54% P_2O_5 . The effect of surfactants on the defluorination process in the further concentration of WPPA to polyphosphoric acid (PPA) will also be discussed. It was determined that resulting PPA contained 63.5-64.5 % P_2O_5 and 0.03-0.06% F.

These methods were tested in the industrial environment.

Wet-process phosphoric acid (WPPA) is one of the basic products needed for the production of phosphoric and compound fertilizers. At the present time the evaporation of WPPA is basically carried out in units with heat transfer through a heating surface. The most commonly used in industry are the evaporators with an outboard heated chamber (VEA) [1,2]. The process of concentrating phosphoric acid is fairly energy consuming: the consumption of steam is about 3t/t P_2O_5 . The existing means of improvement the process of concentrating are connected with a growth of productivity by increasing the reliability of VEA, modifying the concentration process itself, in particular, under the effect of pressure, and developing methods of reducing deposits. However, the concentrated phosphoric acid contains a significant amount of impurities (0.6-0.8%F, 1.2-1.4% R_2O_3). Combining the processes of concentrating the acid and deep defluorination leads to even greater energy costs (steam consumption about 3.5 ton per 1 ton P_2O_5). [3,4]. There is also additional treatment of the acid with steam or a steam-gas mixture and the addition of diatomaceous earth [5]. As a result, the content of fluorine in the concentrated acid decreases to 0.10-0.15%.

In a study of the effect of the composition of phosphoric acid on its defluorination during evaporation, it was established that the presence of alkali metals in any stage of evaporation does not have a significant effect on the degree of defluorination. However,

divalent and trivalent metals inhibit the separation of fluorine compounds into the gas phase.

Since the reduction of water activity, the increase of viscosity, and surface tension are determining factors in concentrating WPPA, it is expedient to be more concerned with the effect of surfactant on the thermal-physical and physical-chemical properties of WPA. Earlier we showed that the addition of a surfactant to phosphoric acid (28% P_2O_5) leads to a change of its physical-chemical and surface properties [6,7]. Thus, the surface tension decreases, the electrical conductivity increases, and the viscosity of the system decreases. We have proposed a method of concentrating WPPA with the use of surfactants, which makes it possible to reduce energy costs of the evaporation and final concentration of fluorine in the concentrated acid.

Tests of this method were carried out under industrial conditions. The process of concentrating WPPA (to 54%) was carried out both without and with surfactant. The vacuum evaporator was operated for 12 days without surfactants. Average data are shown in Table 1. Then the experiments with the surfactant were started without washing the evaporator. The surfactant was continuously dispensed in the form of a 1-2% aqueous solution to the initial acid in the receiver before being sent to the evaporator. The concentration of surfactant in the acid was about 0.002 % (with respect to the initial WPPA). The results of the tests, which were carried out in correspondence with the research technique, are given in Table 1 and 2. Each shift duration was 8 hours. Analysis of the data in Table 1 and 2 shows that in the presence of surfactant there is an increase in the throughput of the evaporator - from 4.8 (without surfactant) to 5.7 t P_2O_5/h - and a reduction of the specific consumption of steam - from 1.20 to 0.92-1.08 t steam/t H_2O . The throughput of the evaporator (about 5.3-5.7 t/h) practically did not

Table 1

Description of Process of Concentrating in the Absence and Presence of Surfactant

Shift's number	Vacuum, MPa	Temp., before heating chamber, °C	Steam flow rate, t/h	Amount of WPPA with respect to 100%P ₂ O ₅ , t	Concentration of WPPA C/C _c , %	Throughput t P ₂ O ₅ /h	Amount of evaporated water, t	Specific consumption of steam, t _{steam} /t H ₂ O	Viscosity of connect. WPPA at 70°C 10 ⁴ m ² /sec	C P ₂ O ₅ in liquid phase of absorber, %
Average without surfactant	0.082	89	8.0	36.5	29.8/52.0	4.8	47.9	1.2	6.62	0.008
1	0.081	81	8.0	66.9	31.6/50.1	8.3	78.2	0.96		0.003
2	0.083	82	7.5	40.9	28.2/53.0	5.1	67.9	0.98	6.15	0.003
3	0.081	85	9.6	47.4	26.9/52.9	5.9	79.7	0.96		0.003
4	0.081	88	8.8	45.5	-	5.1	24.3	1.08	6.13	-
5	0.083	83	8.5	42.7	28.6/53.1	5.3	68.7	0.99	-	0.003
6	0.082	88	8.6	56.8	32.7/51.8	7.1	64.1	1.08	6.13	0.003
7	0.080	89	8.4	41.3	29.1/53.0	5.7	64.6	1.04	6.17	0.006
8	0.080	88	8.5	48.0	28.7/50.4	6.0	70.0	0.97	-	0.007
9	0.083	89	8.0	46.7	29.0/50.2	5.8	69.3	0.92	6.16	0.001
10	0.081	90	8.0	42.7	28.1/51.2.	5.3	64.6	0.99	6.18	0.002
11	0.080	88	8.1	44.1	29.1/53.0	5.5	68.2	0.95	-	0.003
Average	0.082	86	8.5	46.0	28.9/51.9	5.7	-	1.0	6.14	

increase in the entire period of these tests. This result is due to a decrease of the depression by 2-3 degrees, which is connected with a change of the thermal-physical

Table 2

Effect of Surfactant on Composition on Concentrated and Initial Acids

Shift's number	Concentration in acid, %					
	P ₂ O ₅	SO ₃	F*	CaO	SiO ₂	R ₂ O ₃
1	31.6	2.60	----/1.44	0.34	1.03	3.72
1	52.8	3.34	0.40/0.98	0.54	0.47	5.76
2-4	29.5	3.40	1.15/---	0.22	1.41	0.65
2-4	52.6	---	0.23/0.34	0.48	0.48	1.55
2-4	50.0	---	0.68/0.86	0.52	---	1.92
5-7	28.3	2.25	----/1.84	0.26	0.51	2.32
5-7	51.3	3.34	0.32/0.46	0.68	---	2.63
5-7	50.8	3.62	0.56/0.71	0.69	0.62	2.98
8-10	28.0	2.25	----/1.52	0.26	1.16	2.22
8-10	52.0	3.34	0.28/0.41	0.44	0.68	2.66
8-10	50.6	3.34	0.39/0.64	0.48	0.57	3.12

*Numerator contains data for clarified sample, denominator for stirred sample.

properties of the acid and a decrease by about 7% of the viscosity of the concentrated acid (52%). Along with this, there was a decrease in the concentration of fluorine and sesquioxides in the concentrated acid. Splash entertainment remains at the former level in the presence of the surfactant (the concentration of P₂O₅ in the liquid phase of the absorber was an average of about 0.004%).

Industrial realization of the concentrating method that was developed confirmed a reduction of energy cost for concentration of WPPA (steam consumption reduced by 10%) with a simultaneous deeper defluorination of the acid (the amount of fluosilicic acid that formed increased). Table 3 shows average results of industrial concentrated WPPA production with surfactants and without surfactants. Each process was analysed using industrial data collected during five months.

Table 3

Results of Working the WPA Evaporation Department with surfactant

Characteristics	Without surfactant	With surfactant
Throughout in respect to 100%P ₂ O ₅ , t/h	4.1	4.25
Consumption of steam, cal/t P ₂ O ₅	2.28	2.06
Amount of WPPA. t P ₂ O ₅	33130	34471
Amount of time-washing with respect to time-working	24.4	17.4

Industrial production also shows the increase to 28% time of running evaporators between washing.

To determine the possibility of PPA production (63 - 65% P₂O₅) by vacuum evaporation using surfactants, we investigated the concentration of phosphoric acid in the industrial vacuum evaporator. The solution of surfactant was added to the initial WPPA, which contained 50-52% P₂O₅. One phosphoric acid tank was used for initial acid mixing with surfactant and the other tank served for evaporator feeding. Each tank volume was 160m³. The initial acid contained 50,6-52.1% P₂O₅, 0.45-0.68% F, 2.7-2.8%R₂O₃, 3.4-3.7 SO₃, and 2.8-3.1% suspended matter.

The production of PPA takes place in a stable regime with parameters shown in Tables 4 and 5. The resulting PPA contained 63.3-64.5% P₂O₅, 0.03-0.06% F, 3.9% R₂O₃, 3.0-4.7% SO₃, and 0.4-0.6% suspended matter.

Table 4

Operating Parameters of the Evaporator

Characteristics	Without surfactant	With surfactant
Steam pressure, MPa	0.22	0.22
Steam rate, t/h	3.0	2.8 - 3.1
Vacuum in evaporator, MPa	0.08	0.084-0.087
Concentration of PPA, % P ₂ O ₅	59.9	63.5 - 64.8
Fluorine concentration in PPA, %	0.2 - 0.4	0.03 - 0.06
Concentration of P ₂ O ₅ in fluosilicic acid, %	0.006	0.003 - 0.005
Throughput in respect to 100%P ₂ O ₅	2.2	2.1 - 2.3

These results show that using standard graphite heating chamber maximum phosphoric acid concentration without surfactants is only 60% P₂O₅ while up to 65% P₂O₅ acid can be produced in the presence of surfactants.

When we used initial acid containing 0.4 % suspended matter and steam pressure 0.25 MPa, throughput had been increased to 4.2 t/h P₂O₅ and the concentration of PPA had been 64.5- 64.8% P₂O₅. A comparison of the boiling points of the acid containing 63-64.5% P₂O₅ with and without the addition of surfactants at correspondingly with the values given in Table 5 shows a reduction of the boiling points by 5-7 degrees when surfactant added.

Table 5
 Technological Regime of Production of PPA in a Vacuum
 Evaporator in the Presence of Surfactants

Vacuum, MPa	Temperature of heating chamber, °C	Steam rate, t/h	Throughout , t/h	P ₂ O ₅ concentration , %
0.084	120	3.0	2.2	59.9
0.087	120	3.0	2.1	63.2
0.087	120	3.0	2.1	63.3
0.085	123	2.5	2.1	63.1
0.085	120	3.0	2.3	63.1
0.085	120	3.0	2.1	63.1
0.085	120	3.1	-	63.1
0.085	121	3.0	2.1	62.9
0.084	120	3.2	2.1	62.9
0.086	119	3.2	2.1	63.0
0.085	120	3.0	2.1	62.8
0.086	118	3.2	2.1	62.9
0.087	120	3.0	2.1	63.1
0.087	121	3.0	2.1	63.5
0.087	122	2.8	2.3	63.1
0.087	123	2.8	2.1	64.8
0.087	122	2.8	2.1	64.5
0.087	121	2.9	2.1	64.2
0.087	119	3.0	2.3	64.0
0.087	119	2.9	2.1	62.8

PPA produced by the above technology contains less fluorine at the same P₂O₅ concentration than the same acid produced by submerged combustion or vacuum evaporation in the absence of surfactants. Also, the reduction of P₂O₅ content in the gas phase after vacuum evaporator increases the purity of fluosilicic acid which can be reprocessed to high-quality fluorine products, for example in this case into aluminum fluorid

It can be seen from Fig. 1 that the separation of fluorine is more intensive in the presence

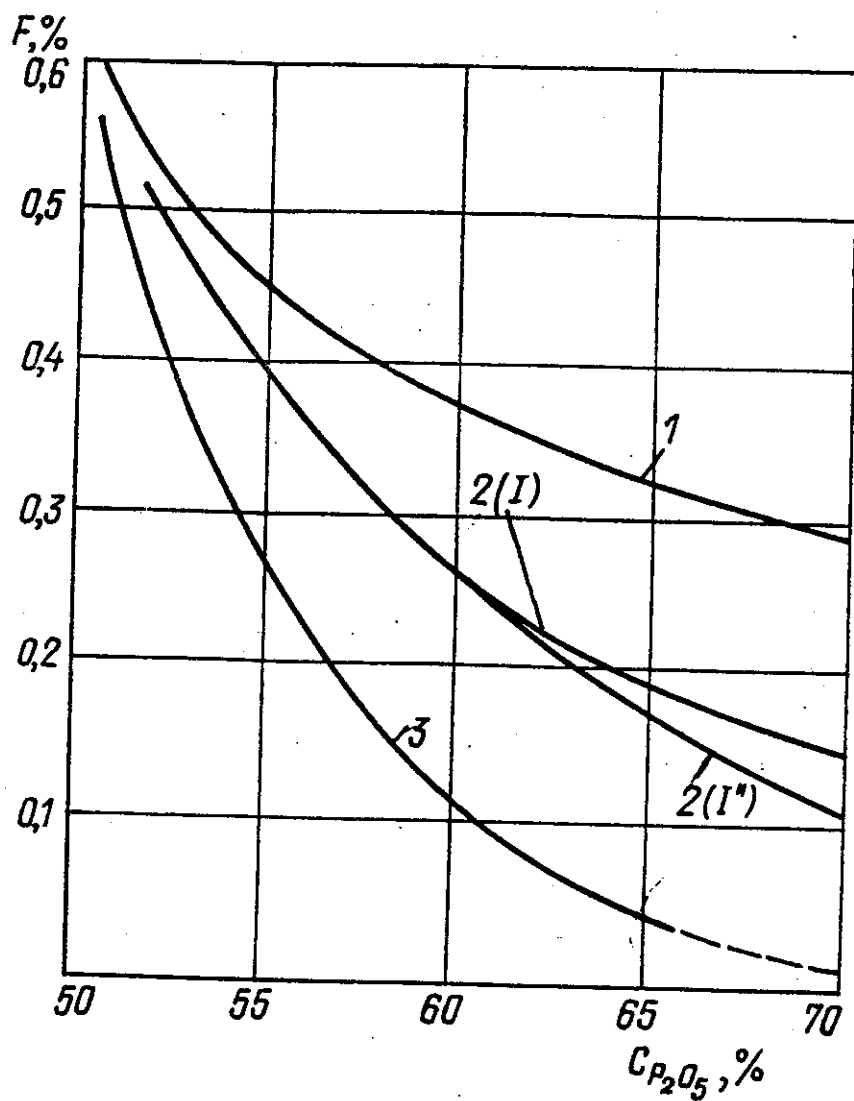


Fig. 1 Dependence of concentration of fluorine in acid on acid concentration for different methods of concentration: 1.) vacuum concentration in the absence of surfactant; 2', 2'') fired evaporators in one or two stages, respectively [8]; 3) vacuum concentration using surfactant by the describe method.

of a surfactant during vacuum evaporation of the acid than under other conditions.

Here the P to F ratio varies in a wider range (400:1) - (900:1) than in PPA that contains up to 70% P_2O_5 ((150:1) - (200:1)).

Thus, the theoretical possibility of producing PPA with addition of surfactants in vacuum evaporators with graphite hearing chambers was demonstrated in a period of industrial tests. This technology makes feasible a zero-waste, ecologically harmless process for production of PPA with excellent technical-economic characteristics on the basis of the existing concentration departments of wet-process phosphoric acid plants.

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