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Synthesizing copper phosphide in interacting of elemental phosphorus with copper (II) oxide in aqueous solutions

The article deals with a possibility of the copper phosphide synthesis by interaction of copper (II) oxide and elemental phosphorus in the water solutions. The method of multifactorial experiment planning was used for more complete assessment of the influence of various factors on the copper phosphide yield, in particular, the concentration of phosphoric acid, the solution temperature, the process duration, the stirring rate and the weight ratio of copper oxide and phosphorus. The target product was identified by the chemical, X-ray phase and electron-optical analyses. Based on the experimental data, taking into account the significant particular functions, a multifactorial generalized equation for the output of copper phosphide was obtained. The equation is used to find the optimal conditions for the copper phosphide synthesis. The partial point dependences of the product yield on the studied factors show that they have a real impact on the process, and the mathematical models are adequate. The yield of copper phosphide is 95.1 %, which is in good agreement with the calculated data (96.5 %). The proposed method of obtaining copper phosphide in interacting of elemental phosphorus with copper (II) oxide in aqueous solutions can be used for industrial large-tonnage synthesis of copper phosphide and phosphoric acid. In this case, the proposed method does not involve appreciable costs for the production re-equipment.

Keywords: elemental phosphorus, copper phosphide, mathematical planning, generalized multifactor equation.

Introduction

Copper-phosphorus alloys are widely used in a number of technological processes in non-ferrous metallurgy. They are used to deoxidize copper, to make phosphorous bronzes, to obtain solders, as well as modifiers of silumin. Today according to some data the demand for copper phosphide in the world market is estimated at 20–30 thousand tons per year [1].

Traditionally copper phosphide is mainly obtained by direct action of copper powder on elemental red phosphorus at very high temperatures [2; 205; 3, 4; 158–161]. However direct fusion of metals with phosphorus is hampered by the high elasticity of phosphorus vapor that causes contamination of the resulting phosphides with the components of the crucible material and the furnace lining.

It is known that at present copper phosphide is obtained in interacting of the copper sulfate solution with phosphate sludge according to the method described in [5].

The basis for obtaining copper phosphide is the reaction of phosphorus interaction with the copper sulfate solution that is represented in equation (1)

$$4P + 6CuSO_4 + 9H_2O \rightarrow 2Cu_3P + 2H_3PO_4 + 6H_2SO_4 \quad (1)$$

However despite the simplicity of the technological design this method has several disadvantages: firstly, copper phosphide obtained by this method contains sulfate sulfur, the presence of which affects dramatically the quality of the product obtained; secondly, the secondary waste is generated in the form of a mixture of sulfuric and phosphoric acids in the filtrate requiring respectively further processing that is associated with additional operations and costs.

In this regard the development of fundamentally new, cheap, and environmentally friendly technologies for synthesizing metal phosphides is a very topical issue.

In order to obtain pure copper phosphide and to simplify the process we carried out preliminary experiments and showed the possibility of obtaining copper phosphide in interaction of elemental phosphorus with copper (II) oxide in the solution of phosphoric acid.

Method

For a more complete assessment of the various factors influence on the yield of copper phosphide studies were carried out according to the method of rational experiment planning [6; 37; 7; 116].

We studied the effect of various factors on the yield of copper phosphide, in particular, the concentration of phosphoric acid, the solution temperature, the process time, the stirring rate and the weight ratio of copper oxide and phosphorus (Table 1).

Table 1

Factors studied and their levels

Factor	Level				
	1	2	3	4	5
X_1 is the concentration of phosphoric acid, g/l	50	100	150	200	250
X_2 is the temperature *t*, ºC	45	55	65	75	85
X_3 is duration, h	0.5	1.0	1.5	2.0	2.5
X_4 is the stirring rate, W, rev/min	800	900	1000	1100	1200
X_5 is the weight ratio, CuO/P	2.5	3.0	3.5	4.0	4.5

The experiments were carried out in a thermostated cell with the capacity of 300 ml equipped with an agitator with the adjustable rotation speed. Elemental white phosphorus and copper (II) oxide were introduced into the heated phosphoric acid solution and mixed using a mechanical stirrer.

In accordance with the planning matrix for 5 factors there were carried out 25 experiments for each factor with variations at 5 levels. The experiment plan and results are shown in Table 2.

Table 2

Experiment plan and results of elemental phosphorus interaction with copper (II) oxide in the phosphoric acid solution

No.	X_1	X_2	X_3	X_4	X_5	Y_E	Y_P
1	50	45	0.5	800	2.5	0.73	0.74
2	50	65	1.5	1000	3.5	0.80	0.79
3	50	55	1.0	900	3.0	0.81	0.82
4	50	85	2.5	1200	4.5	0.89	0.84
5	50	75	2.0	1100	4.0	0.82	0.86
6	150	45	1.5	900	4.5	0.66	0.65
7	150	65	1.0	1200	4.0	0.82	0.78
8	150	55	2.5	1100	2.5	0.83	0.85
9	150	85	2.0	800	3.5	0.89	0.88
10	150	75	0.5	1000	3.0	0.87	0.88
11	100	45	1.0	1100	3.5	0.79	0.79
12	100	65	2.5	800	3.0	0.84	0.83
13	100	55	2.0	1000	4.5	0.84	0.83
14	100	85	0.5	900	4.0	0.79	0.82
15	100	75	1.5	1200	2.5	0.78	0.77
16	250	45	2.5	1000	4.0	0.76	0.76
17	250	65	2.0	900	2.5	0.74	0.77

Continuation of Table 2

No.	X_1	X_2	X_3	X_4	X_5	Y_E	Y_P
18	250	55	0.5	1200	3.5	0.74	0.79
19	250	85	1.5	1100	3.0	0.89	0.83
20	250	75	1.0	800		0.90	0.82
21	200	45	2.0	1200	3.0	0.79	0.76
22	200	65	0.5	1100	4.5	0.75	0.83
23	200	55	1.5	800	4.0	0.87	0.86
24	200	85	1.0	1000	2.5	0.88	0.83
25	200	75	2.5	900	3.5	0.76	0.76

Note. $X_1…X_5$ are the factors studied; Y_E is an experimental value of the recovery degree; Y_P is calculated according to Protodyakonov's equation.

The phosphorus sample mass in all the experiments was constant and equal to 0.8 g. After a specified period of time the solid and liquid phases were separated by filtration and residual copper was determined in the filtrate, copper and phosphorus in the sediment [8; 715, 865].

Results and Discussion

According to X-ray phase, electron-optical and chemical analyses the product of the reaction is copper phosphide.

Electron microscopy of copper phosphide shows that the maxima in the electron diffraction pattern of phosphide at 2.68; 2.40; 2.17; 1.75; 1.57 coincide with the X-ray phase analysis data 2.17 (26); 2.40 (23); 1.75 (34) (Fig. 1, 2).

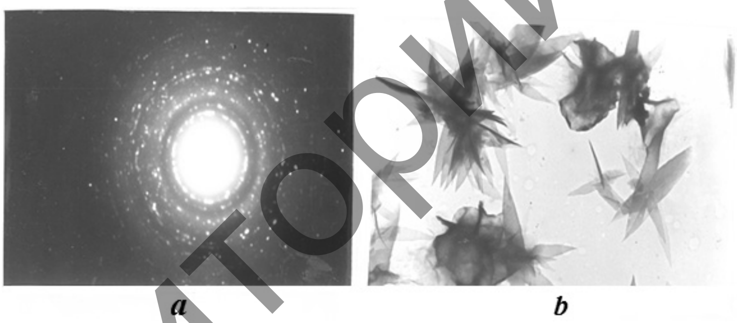

Figure 1. Electron-diffraction pattern (*a*) and microphotography (*b*) of copper phosphide (×7000)

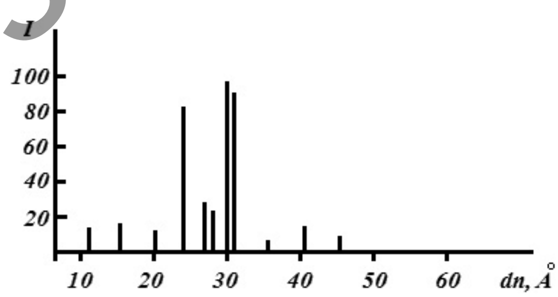

Figure 2. Bar X-ray pattern of copper phosphide

The partial point dependences of the target product yield on the studied factors are presented in Figures 3–5. The equations describing their coefficients are listed in Table 3. The t_R> 2 signification shows that all the factors studied have a real impact on the process, and the resulting mathematical models are adequate [6; 37; 7; 116].

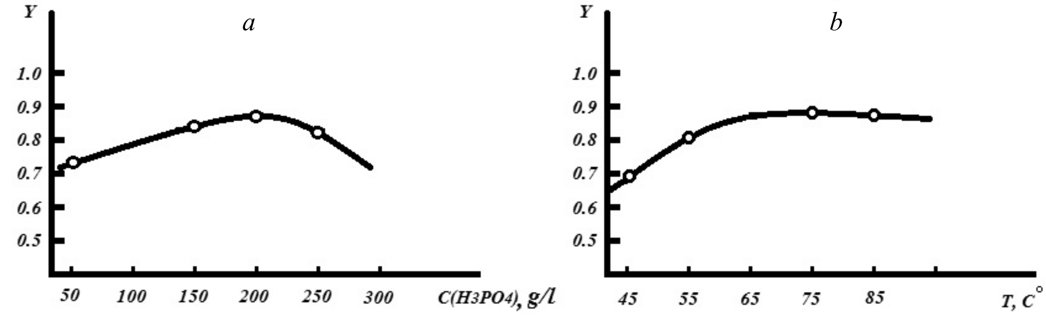

Figure 3. Copper phosphide yield dependence on the concentration (*a*) and the temperature (*b*) of the solution

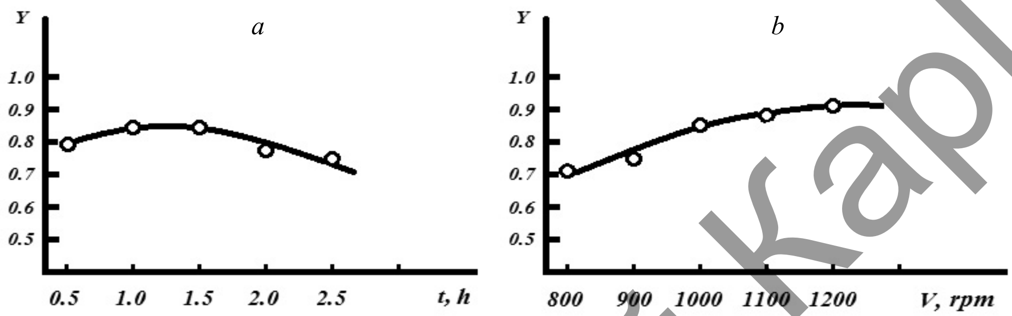

Figure 4. Copper phosphide yield dependence on the duration (*a*) and the stirring rate (*b*) of the process

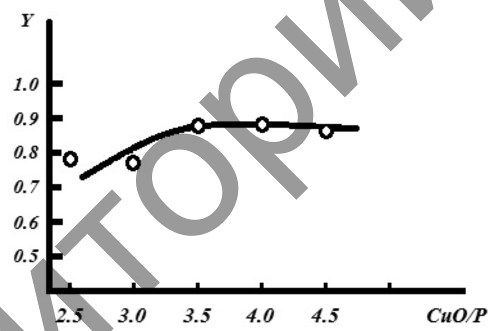

Figure 5. Copper phosphide yield dependence on the copper oxide/phosphorus ratio

The nature of the obtained partial dependences can be explained as follows. With increasing the concentration of phosphoric acid to 200 g/l (Fig. 3*a*) the copper phosphide yield increases by the reaction

$$4P + 5CuO + 3H_2O \xrightarrow{H_3PO_4} Cu_5P_2 + 2H_3PO_4. \quad (2)$$

Further increasing the concentration of electrolyte leads to decreasing the product yield. This is probably due to the fact that solubility of copper oxide in concentrated solutions of phosphoric acid decreases with increasing the concentration [9; 283–285].

Table 3

Correlation coefficients R and their significations t_R for private functions

Function equations	*R*	t_R	Function signification
$Y_1 = 3.64 \times X_1^{0,0189} - 3.17$	0,77	3,36 > 2	significant
$Y_2 = -1,85 \times 10^{-4} \times X_2^2 + 0,0296 \times X_2 - 0,292$	0,98	3,61 > 2	significant
$Y_3 = -5,31 \times X_3^2 + 0,14 + 0.736$	0,78	3,78 > 2	significant
$Y_4 = 9,62 \times 10^{-29} \times X_4^{8,84} + 0,766$	0,80	3,83 > 2	significant
$Y_5 = -9,61 \times X_5^2 + 1,19 \times X_5 - 2,79$	0,73	3,33 > 2	significant

As the results of chemical analysis show one half of the initial phosphorus is bound to copper to form copper phosphide, and the remainder goes to the solution in the form of phosphate ions.

As it can be seen from Figures 3*b*, 4*b* the maximum dependence of the copper phosphide yield on the temperature and stirring rate is at the temperature of 65 ºC and the stirring rate of 1100 rev/min. Further increasing the temperature and stirring rate does not increase the yield of the target product.

The degree of copper phosphide formation dependence on the duration of the process is also maximum when the duration of the process is 1.5 hours (Fig. 4*a*).

With increasing the duration of the process the degree of copper phosphide formation falls. Decreasing the product yield is apparently caused by partial dissolution of freshly formed copper phosphide.

As it can be seen from Figure 5 increasing the weight ratio of copper oxide when phosphorus is more than 3.5–4.0:1 is not advisable, since there is no significant increase in the product yield. Based on the experimental data taking into account the significant particular functions a multifactor generalized equation for the output of copper phosphide is obtained:

$$Y = Y_1 + Y_2 + Y_3 + Y_4 + Y_5 - 3{,}25\,. \quad (3)$$

After substituting partial dependences, the generalized equation has the form:

$$\begin{aligned} Y_c &= 3.64 \times X_1^{0.0189} - 3.17 - 1.85 \times 10^{-4} \times X_2^2 + 0.0296 \times X_2 - \\ &-0.292 - 5.31 \times 10^{-2} \times X_3^2 + 0.14 + 0.736 + 9.62 \times 10^{29} \times X_4^{8.84} + \\ &+0.766 - 9.61 \times 10^{-2} \times X_5^2 + 1.19 \times X_5 - 2.79 - 3.25. \end{aligned} \quad (4)$$

The obtained generalized multifactor equation was used to find the optimal conditions for obtaining copper phosphide. The calculated optimal process conditions had the following values: the phosphoric acid concentration 200 g/l, the temperature 65 ºC, the process time 1.5 hours, the stirring rate 1100 rev/min, CuO:P weight ratio was 3.5:1. Under these conditions the calculated yield of copper phosphide is 96.5 %.

To test the multifactor equation a control experiment was performed in the optimal mode.

The yield of copper phosphide is 95.1 %, which is in good agreement with the calculated data.

According to the results of the tests it was established that the use of copper oxide as a copper donor eliminates all the main disadvantages inherent in the above mentioned vitriol technology [5]. Below there are given the component compositions of copper phosphide samples obtained by the vitriol and the proposed oxide technologies (Table 4).

Table 4

Data of the component compositions of copper phosphide samples obtained by the vitriol and the proposed oxide technologies

Requirements of standard specifications 113-25-04-06-88. Mass. share, %			The average component composition in (%) of copper phosphide obtained by the vitriol technology					The average component composition in (%) of copper phosphide obtained by the oxide technology				
Grade	A	B	1	2	3	4	5	1	2	3	4	5
Cu	50–80	50–80	53.87	54.04	54.56	52.02	53.25	53.02	53.42	59.21	58.20	53.40
P_4	7–14	6–14	5.1	9.49	10.1	11.18	6.2	13.82	14.05	14.10	13.90	14.01
S no more	1,0	8,0	2.63	2.45	2.47	2.99	2.21	0.084	0.079	0.095	0.089	0.065
F	1–3	8,0	0.12	0.17	0.23	0.37	0.30	0.048	0.039	0.055	0.042	0.051
Fe	1,0	1,6	0.42	0.26	0.24	0.29	0.32	0.04	0.03	0.05	0.03	0.04

Conclusions

Thus according to the method of rational experiment planning there was studied the impact of various factors on obtaining copper phosphide in interacting of elemental phosphorus with copper (II) oxide in the solution of phosphoric acid. It is shown that the yield of copper phosphide really depends on the concentration and the temperature of the solution, the duration of the process, the stirring rate and the copper oxide/phosphorus weight ratio.

The proposed method of obtaining copper phosphide can be successfully used for industrial large-tonnage synthesis of copper phosphide and phosphoric acid wherein the proposed method does not involve appreciable costs for the production re-equipment.

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Б.Ш. Сарсембаев, К.С. Ибишев, М.М. Доспаев

Сулы ерітінділерде элементарлы фосфорды мыс (ІІ) тотығымен әрекеттестіру арқылы мыс фосфидін алу

Мақалада элементарлы фосфордың сулы ерітінділерінде мыс (ІІ) тотығымен өзара әрекеттесуі арқылы мыс фосфидін алу мүмкіндігі зерттелген. Мыс фосфидінің шығымына әртүрлі факторлардың, атап айтқанда фосфор қышқылының концентрациясы, ерітінді температурасы, процестің ұзақтығы, араластыру жылдамдығы және мыс оксиді мен фосфордың салмақтық арақатынасының әсерін толығырақ бағалау үшін тәжірибені математикалық жоспарлаудың көпфакторлы әдістемесі қолданылды. Мақсатты өнім химиялық, рентгенфазалық және электронды-оптикалық анализдер арқылы анықталды. Маңызды жеке функцияларды ескере отырып, тәжірибелік деректер негізінде мыс фосфиді шығымының көпфакторлы жалпылама теңдеуін алдық. Ол өнімді алудың оптималды жағдайларын анықтау үшін қолданылды. Қарастырылған факторларға мыс фосфиді шығымының тәуелділіктері олардың процеске нақты әсерін және математикалық үлгінің дұрыстығын көрсетті. Мыс фосфидінің шығымы 95,1 % құрады, бұл есептеулік деректерге сәйкес келеді (96,5 %). Ұсынылатын мыс фосфидін алу әдісі мыс фосфидін және фосфор қышқылын өнеркәсіптік ірі тоннажды синтездеу үшін қолданылуы мүмкін. Сонымен қатар, бұл өндірісті қайта жабдықтауға елеулі шығындарды талап етпейді.

Кілт сөздер: элементарлы фосфор, мыс фосфиді, математикалық жоспарлау, жалпылама көпфакторлы теңдеу.

Б.Ш. Сарсембаев, К.С. Ибишев, М.М. Доспаев

Синтез фосфида меди при взаимодействии элементарного фосфора с оксидом меди (II) в водных растворах

В статье исследована возможность получения фосфида меди при взаимодействии элементарного фосфора с оксидом меди (II) в водных растворах. Для более полной оценки влияния различных факторов на выход фосфида меди, а именно: концентрации фосфорной кислоты, температуры раствора, продолжительности процесса, скорости перемешивания и весового соотношения оксида меди и фосфора использовали методику многофакторного математического планирования эксперимента. Целевой продукт идентифицировали с помощью химического, рентгенофазового и электронно-оптического анализов. На основании экспериментальных данных с учетом значимых частных функций было получено многофакторное обобщенное уравнение выхода фосфида меди, которое использовали для нахождения оптимальных условий получения продукта. Частные точечные зависимости выхода фосфида меди от рассмотренных факторов показали их действительное влияние на процесс и адекватность математической модели. Выход продукта составил 95,1 %, что хорошо согласуется с расчетными данными (96,5 %). Предлагаемый нами метод получения фосфида меди может быть использован для промышленного крупнотоннажного синтеза фосфида меди и фосфорной кислоты. При этом он не требует существенных затрат на переоборудование производства.

Ключевые слова: элементарный фосфор, фосфид меди, математическое планирование, обобщенное многофакторное уравнение.

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