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Purification of phosphorus by a zero pollution zone melting technique

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ABSTRACT

This article introduces an efficient, low cost, and clean (zero pollution) zone melting phosphorus purification technique. We have successfully removed arsenic from solid phosphorus by melting a narrow region and making the resulting liquid zone travel slowly through a relatively long ingot of phosphorus. This technique can reduce arsenic concentration in solid phosphorus from 100 ppm to 10 ppm in a specific condition. Purified solid phosphorus can be used to produce 85% phosphoric acid with arsenic concentration of 2.8 ppm as an additive in the food industry (lower than both the Food and Drug Administration standard (FDA) and the Food Chemicals Codex standard (FCC) of 3 ppm for food grade phosphoric). We applied the phase-field model to establish a system of PDEs and numerically obtained a continuous melting zone moving along with the heater.

1. Introduction

Phosphorus, an element that is abundant in various mineral rocks in oxide form, is an essential nutrient for all life forms. It plays a significant role in metabolism such as forming backbones of DNA and RNA as well as making up the cell walls and bones of vertebrates. In the human body, it is the sixth most common element accounting for 1.2 g per kg-body weight [1–3]. Aside from its presence in the form of hydroxyapatite [4] in the bone structure, it is a key component of adenosine triphosphate (ATP) which acts as the primary energy carrier within all living cells. It is involved in every literal beat of the heart and each slight movement of a muscle, requiring first an in-take and then a natural re-synthesis of the ATP molecule; interruption of this cycle may lead to cessation of life processes. The main source of phosphorus for human beings and animals is food intake. Therefore, it is advisable to add a certain amount of phosphorus into livestock forage so that the human body can obtain it through meat and other kinds of food processed from livestock. Alternatively, phosphorus can be directly added into food products, such as beverages.

Among the ingredients of soft-drinks (such as Coca-Cola) is phosphoric acid, which is indicated representatively by the label of a coca cola bottle. As Coca-Cola becomes increasingly popular, the amount of food-grade phosphorus increases in demand. A challenge faced by the food industry is minimizing the arsenic concentration in phosphorus. It is well known that phosphorus and arsenic co-exist because they are both group V elements and share similar chemical properties. Therefore, it is difficult to separate them through simple chemical methods. High arsenic concentrations could increase the risk of several types of cancer, such as skin and lung cancer [5]. Industrial grade phosphorus contains arsenic of the concentration ranging from 80 to 140 ppm (sometimes even 300 ppm). According to both the Food and Drug Administration standard (FDA) [6] and the Food Chemicals Codex standard (FCC) [7], the arsenic concentration in food grade phosphoric acid (85%) should be below 3 ppm.

Solid phosphorus (melting point of 44.2 °C) is extremely flammable when exposed to air. The lack of a conventional solvent for phosphorus makes the purification process difficult. The conventional methods are all in high energy consumption and may cause environmental pollution. Herein, we summarize the main disadvantages of conventional purification methods: (1) *Vacuum distillation* [8]: Excessive iodine (around 10,000 times in excess) is added to the white phosphorus by the stoichiometric amount. Iodine would then react with arsenic to form arsenic iodide. Arsenic iodide has a much higher boiling point than phosphorus and, thus, arsenic can be separated from phosphorus by this method. Most of the arsenic can be separated from phosphorus through the vacuum distillation by the difference in boiling point. The disadvantage is that this process would produce large amounts of iodine, which is both corrosive and poisonous. This method is, therefore, very dangerous to operate. (2) *Liquid–liquid extraction* [9]: Crude yellow phosphorus is first mixed with the oxidant, nitric acid. Most of the arsenic inside the phosphorus would react to form arsenic acid but only part of the phosphorus would react to form phosphoric acid. When the mixture is heated to melting point, or when more phosphorus is melted, liquid phosphorus and nitric

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acid are separated into two layers by the difference of specific gravity. Most of the arsenic acid is dissolved into nitric acid due to different selectivity and thus separation of the arsenic can be done by extracting the liquid phosphorus. However, this method is not widely used because it uses nitric acid as a solvent, which is a strong acid and highly corrosive and highly oxidant. (3) *Fractional distillation* [10]: Impure phosphorus is continually passed through a heat exchanger and heated to vaporize a portion of the phosphorus at a temperature not above 200 °C. The materials with a large boiling point difference to achieve phosphorus vaporization will be separated in a disengaging zone, while arsenic will be separated in a fractionating zone due to the vapor–liquid equilibrium. Distillation is both capital and labor intensive, and also leaves a distillation residue product that is much higher in arsenic and other heavy metals due to the concentration caused by the distillation. (4) *Mixing and extraction* [11]: The purification of yellow phosphorus can be done in this process by mixing liquid yellow phosphorus with active carbon and then separating the purified phosphorus from the spent active carbon containing adhering phosphorus. The spent active carbon is mixed with sufficient liquid phosphorus to form slurry, which is pumped to a disposal zone. The disposal of the spent active carbon can cause several problems. For example, the active carbon spent gives rise to a useless and insignificant consumption of phosphorus. (5) *Phase separation* [12]: Impure white phosphorus mixed with an aqueous suspension of a purifying amount of active charcoal can be used to separate phosphorus from the separation funnel due to different phases. The mixture of aqueous impurities is first separated into a settled phase consisting essentially of a spent active charcoal and phosphorus-containing phase and an aqueous phase. Then the phosphorus-containing phase and thus, the purified liquid white phosphorus can be separated from another separation. However, the production of the active charcoal causes much pollution as the acid is involved and heavy metal is produced. (6) *Oxidation* [13]: The purification of crude yellow phosphorus can be treated by oxidizing those with mixed acid of sulfuric acid and nitric acid. The crude yellow phosphorus is first pretreated by alkali leaching with ammonium carbonate. Then, the reactant is oxidized with mixed acid of sulfuric acid and nitric acid. The purified phosphorus can be found after washing with hot water. The strong acid, sulfuric acid and nitric acid, which is highly corrosive, and strongly oxidizing agent is used as the oxidant. This can result in water pollution when disposing them into the sea. The loss of phosphorus in reaction forming phosphorus acid would also occur.

As seen above, all the methods summarized have significant disadvantages, such as high energy consumption, hazardous operation-conditions (toxic solvent and vapor), and low yield. The zone melting process developed in this study for phosphorus purification is clean, chemical free, fast, and energy efficient. It is absolutely a zero pollution process. Apart from the food industry, high purity phosphorus is also important in many other industries, especially in the electronic industry.

2. Experiments and results

The main apparatus used for zone melting consists of a heater that can move slowly along the solid sample bar to be purified. When the purification starts, the heater heats a narrow band of the sample to the melting point and a melting zone is formed. Only the specific area heated by the heater can be melted. As the heater travels along the sample, the melting zone moves correspondingly. After the heater passes, the melting zone cools and solidifies. During the solidification process, impurities are segregated into the liquid-phase region. Fig. 1 illustrates the experimental setup of the zone melting purification process [14].

All the operations were carried out in water in a stainless steel tank, because phosphorus is very flammable in air. We set the diameter of the phosphorus sample bar to be 10 mm and the width of the heater to be 40 mm. The length of the phosphorus sample bar was chosen to be 400 mm.

To verify the effectiveness of this process, we need to quantify the concentration of arsenic (As) in solid phosphorus before and after the zone melting purification. Inductively coupled plasma atomic

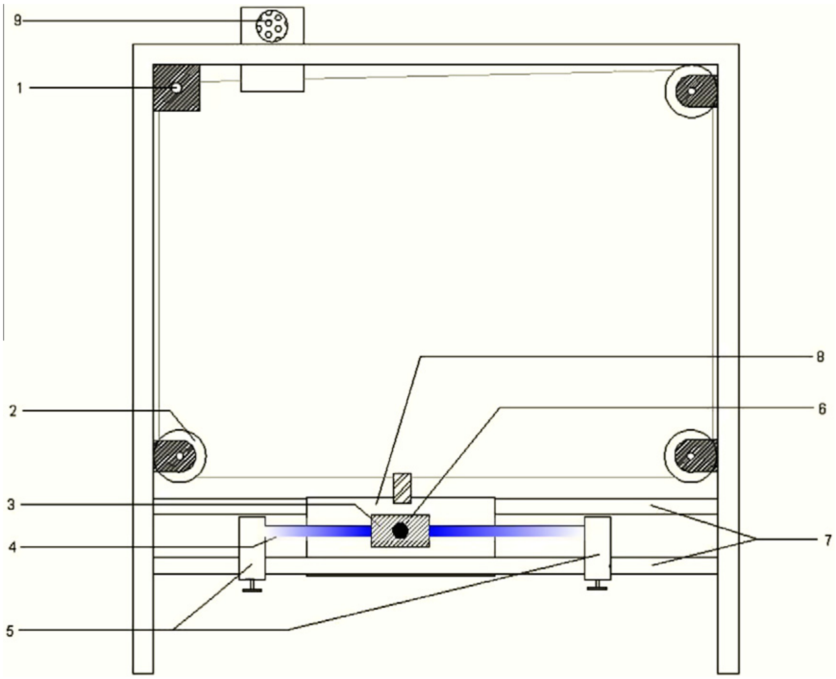

Fig. 1. The design of the apparatus for the zone melting purification of phosphorus: (1) step motor, (2) pulley, (3) heater for zone melting, (4) phosphorus bar, (5) plastic blocks, (6) heater, (7) bar 1 and bar 2 for fixing the sample holders, (8) back panel, and (9) speed controller.

Table 1
Concentration of arsenic after purification.

Sample weight (g)	Sample volume (ml)	Result from ICP (mg/l)	Conc. of As in solid *P* (mg/kg or ppm)
0.872	100	<0.081	<10

emission spectrometry (ICP-AES) was used in analyzing the trace concentration of arsenic. The procedure is described as follows:

2.1. Sample preparation

First, 15 ml HNO_3 (70%) was poured into a 250 ml flat-bottom boiling flask (FB), followed by weight measurement. The solid phosphorus sample was then put into the boiling flask. Afterwards, the boiling flask was connected to the Jacketed condenser. The phosphorus reacted with HNO_3 (70%) completely. During the reaction, the phosphorus was submerged in the HNO_3 liquid in order to prevent it from reacting with the air. The cooling water should be kept flowing during the whole reaction process. When the reaction was completed, the Jacketed condenser was removed after being rinsed with distilled water. The resulting solution was then transferred from the boiling flask to a 100 ml flask. After that, distilled water was filled into the flask until its standard full capacity.

2.2. Standard solution

The concentration of arsenic in standard solution is 1000 ppm. 0.2 ml and 0.5 ml of the standard arsenic solution was sampled and diluted to 100 ml respectively. Therefore the resulting arsenic concentration should be 2 and 5 ppm.

Making of the stand curve and measuring the concentration of arsenic using ICP-AES.

2.3. Calculation

If we denote the result obtained from ICP-AES as *CAs* (mg/l), the weight of phosphorus as *Wp* (g), and the volume of sampled solution as *Svol* (l), the concentration of arsenic in phosphorus, *A* in the unit of mg/kg or ppm can be extracted from the formula:

$$A = CAs \times Svol/Wp \times 1000.$$

Before the purification process, the arsenic concentration was 100 ppm. According to Table 1, the concentration was reduced to 10 ppm after the zone melting purification process when the velocity of the heater was 1 mm/min and the temperature of the heater was 48 °C. The purified solid phosphorus can be used to produce 85% phosphoric acid as an additive in the food industry, with arsenic concentrations of 2.8 ppm, which is less than 3 ppm and thus fulfills the requirements set by the FDA standard and FCC standard.

3. Mathematical model for the zone melting technique

The phosphorus bar sample is shown in Fig. 2. We denote the width of the heater, which is also the width of the area to be heated, as *d*. The total length of the bar is *L* and the radius is *R*.

We applied a mathematical model to simulate the zone melting process. The model is based on a phase-field model for solid–liquid phase transition [15–18] first established by McFadden et al. [17], as shown below:

$$\frac{1}{M}\phi_t = (K_E + TK_S)\nabla^2\phi - \frac{1}{2}(W_E + TW_S)g'(\phi) + \frac{L_V(T - T_M)}{T_M}p'(\phi) \tag{1}$$

$$c_P T_t + L_V r'(\phi)\phi_t + \frac{1}{2}W_E g'(\phi)\phi_t = \nabla\cdot[k(\phi)\nabla T] + K_E\phi_t\nabla^2\phi \tag{2}$$

where $\phi(x, t)$ is a nonconserved order parameter that indicates the phases, with $\phi = 0$ in the solid phase and $\phi = 1$ in the liquid phase. $T(x, t)$ is the temperature at the position x at time t. $M > 0$ is a mobility coefficient and K_E, $K_S > 0$ are gradient energy coefficients, W_E, $W_S > 0$ are barrier heights for the double well potential function $g(\phi) = \phi^2(1 - 2\phi^2)$ and $p(\phi) = \phi^2(3 - 2\phi)$. $k(\phi)$ permits different thermal conductivities $k_L = k(1)$ and $k_s = k(0)$ in the bulk liquid and solid phases, respectively. The function $r(\phi)$ is assumed to have $r(0) = 0$ and $r(1) = 1$. We choose $r(\phi) = p(\phi)$. L_V is the latent heat per unit volume, c_P is the heat capacity per unit volume, and T_M is the melting point.

The system of equations (Eqs. (1) and (2)) can be derived from the fact that entropy production is positive and the conservation laws for the energy [17–19].

Rescaling $\tilde{x} = x/R,\ \tilde{t} = t/(R^2/\overline{\kappa}),\ u = (T - T_M)/(L_V/c_P)$ in the above equations, we obtain the dimensionless form:

$$\varepsilon\tau\phi_{\tilde{t}} = \varepsilon^2(1 + \alpha u)\tilde{\nabla}^2\phi - \frac{1}{2}(1 + \beta u)g'(\phi) + \lambda u p'(\phi) \tag{3}$$

$$u_{\tilde{t}} + r'(\phi)\phi_{\tilde{t}} + \frac{1}{2}\delta g'(\phi)\phi_{\tilde{t}} = \tilde{\nabla}\cdot[Q(\phi)\tilde{\nabla}u] + \varepsilon^2 \nu\phi_{\tilde{t}}\tilde{\nabla}^2\phi \tag{4}$$

where $\overline{\kappa} = \frac{1}{2}(\kappa_L + \kappa_S)$ is the average of the thermal diffusivities, $\kappa_L = k_L/c_P$ in liquid and $\kappa_S = k_S/c_P$ in solid, $Q(\phi)$ is an interpolating function between dimensionless solid and liquid thermal diffusivities.

Parameters employed in Eqs. (3) and (4) are listed below:

$$\varepsilon = \frac{1}{R}, \quad \lambda = \frac{1}{6l_c}, \quad \tau = \frac{\overline{\kappa}T_M c_P}{6ll_c M L_V^2}, \quad l_c = \frac{T_M\gamma}{L_V^2}c_P,$$

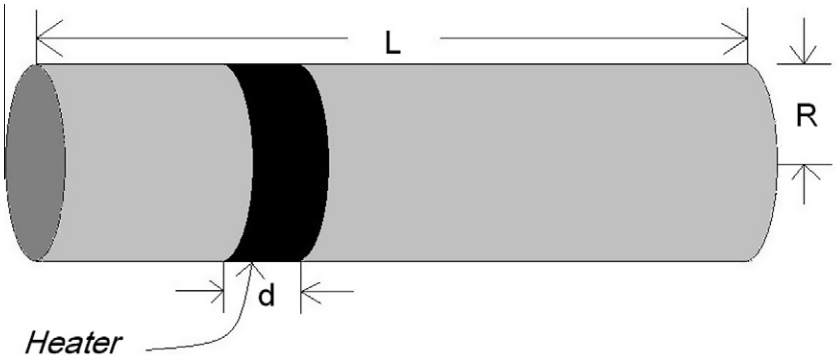

Fig. 2. The phosphorus bar sample.

$$l = \left(\frac{K}{W}\right)^{\frac{1}{2}}, \quad \gamma = \frac{1}{6}(KW)^{\frac{1}{2}}, \quad \mu = \frac{6ML_V l}{T_M},$$

$$K = K_E + T_M K_S, \quad W = W_E + T_M W_S, \quad Q(\phi) = \frac{k(\phi)}{\overline{\kappa} c_P},$$

$$\alpha = \frac{K_S(L_V/c_P)}{K}, \quad \beta = \frac{W_S(L_V/c_P)}{W}, \quad \delta = \frac{W_E}{L_V}, \quad \mu = \frac{K_E}{L_V l^2}.$$

Special forms of the above parameters can be applied based on the asymptotic analysis presented by McFadden et al. [17]:

$$r(\phi) = p(\phi), \quad \frac{1}{Q(\phi)} = \frac{r(\phi)}{Q_L} + \frac{1 - r(\phi)}{Q_S},$$

$$\beta = \nu = 0, \quad \alpha = -\frac{76}{5}\lambda\left(\frac{\kappa_L - \kappa_S}{\kappa_L + \kappa_S}\right), \quad \delta = \frac{\alpha}{\lambda},$$

$$\frac{1}{M} = \frac{c_1 l^2 \overline{\kappa}\left(L_V^2/c_P\right)}{\kappa_L \kappa_S T_M}\left(1 - 4c_2\left(\frac{\kappa_L - \kappa_S}{\kappa_L + \kappa_S}\right)^2\right),$$

where we require $0.0689 < \frac{\kappa_S}{\kappa_L} < 14.5, c_1 = \frac{19}{5}, c_2 = \frac{173}{525}$.

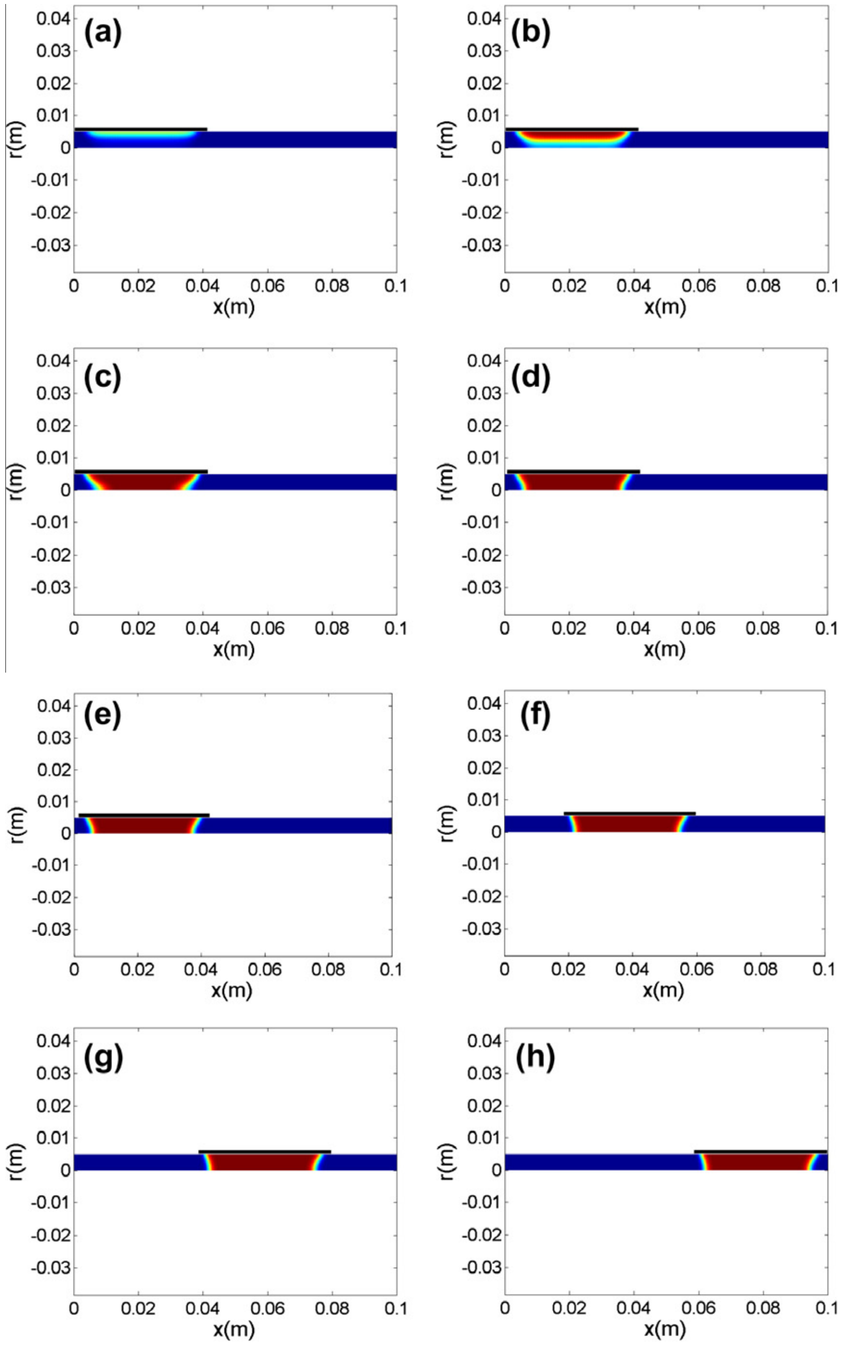

Fig. 3. The numerical simulation snapshots at different time: (a) t = 40 s, (b) t = 80 s, (c) t = 110 s, (d) t = 140 s, (e) t = 180 s, (f) t = 1200 s, (g) t = 2400 s, and (h) t = 3600 s. The black bar represents the heater, the red region stands for the liquid region and the blue one is the solid. The interface between the liquid and solid is represented by the yellow region. The melting time is 108.1 s: (a) and (b) indicate the melting of the outer shell of the phosphorus bar, (c) indicates the complete fusion, and (d)–(h) indicate the moving of the melting zone.

The interface thickness, l, can be prescribed to be 0.1 mm. The total length L is 0.1 m. Other physical constants are: $k_S = 0.235$ W/(m K) [20–22], $k_L = 0.187$ W/(m K) [20–22], $L_V = 9.71 \times 10^6$ J/m^3 [22], $c_P = 3.50 \times 10^5$J/(m^3 K) [22], and $h = 500$W/(m^2 K) which is an averaged value we took from the literature and this value is not sensitive to our numerical evaluation.

The dimensionless boundary conditions are given by:

$$\frac{\partial u}{\partial n} = \frac{hR(T_h - uL_V/c_P - T_M)}{L_V\overline{\kappa}Q(\phi)} \text{ in the heating region,} \tag{5}$$

$$\frac{\partial u}{\partial n} = \frac{hR(T_0 - uL_V/c_P - T_M)}{L_V\overline{\kappa}Q(\phi)} \text{ otherwise,} \tag{6}$$

$$\frac{\partial \phi}{\partial n} = 0. \tag{7}$$

where n is the outward normal vector, h is the convective heat transfer coefficient, T_0 is the environmental temperature, and T_h is the temperature of the heater.

Assuming radial symmetry, the 3-D problem can be reduced to a 2-D problem with a rectangular computational domain $(x, r) \in [0, L] \times [0, R]$.

The explicit finite difference scheme was applied to solve the equations (Eqs. (3) and (4)).

4. Numerical results

Numerically, we investigated several issues related to the purification process and made comparisons with the experimental results. Numerically, quantities of concern are (1) fusion time: the time required for the region under the heater to melt, (2) the velocities of both interfaces, and (3) the lengths of the fusion region with different radii.

In the zone melting experiments, we set the temperature of the water tank to be 25 °C. A set of simulations with different temperatures and velocities of the heater were performed. The melting zone should first be established in the area heated by the heater, and then travel along the phosphorus bar as the heater moves rightwards.

Among our simulation results, Fig. 3 shows that the dynamic melting zone is perfectly established and that the melting zone shifts consistently with the moving heater. The temperature, moving velocity, and length of the heater were set to be 48 °C, 1 mm/min, and 40 mm, respectively. The radius of the phosphorus sample bar was 5 mm. We can see that during the whole process only the region covered by the heater was the melt. As the heater passed, the region that used to be melted solidified again. Both interfaces between the melted and solid regions shifted correspondingly with the heater. The shape of the melted region remained unchanged as illustrated in Fig. 3. Fig. 4 demonstrates the temperature distribution of the melting zone in a 2-D view, which is perfectly bell-shaped as we expected. Fig. 5 shows the fact that the moving velocity of the melting zone is exactly equal to that of the heater, which confirms our observation.

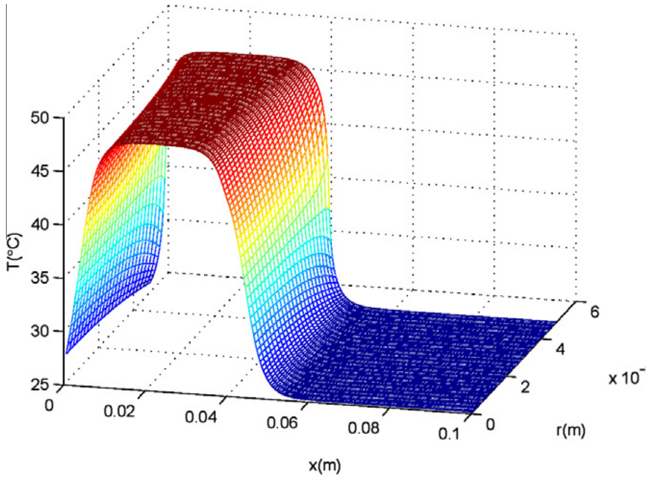

Fig. 4. Temperature in 2-D at the time t = 300 s.

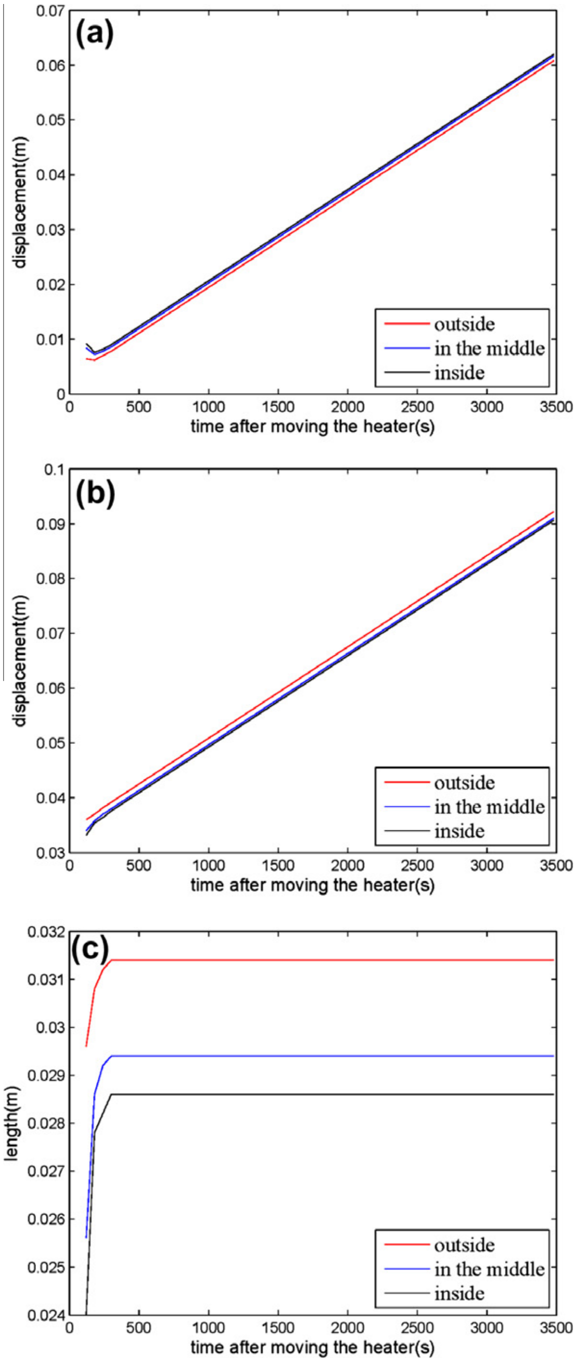

Fig. 5. The moving characteristic of the fusion region: (a) displacement of the left interface, (b) displacement of the right interface, and (c) length of the melting region.

This set of simulation results provides a crucial base for establishing the zone melting process: It provides the reasonable parameters (such as moving velocity, temperature, and length of the heater), under which the melting zone can move along with the heater. This is also consistent with the experimental data.

Furthermore, the mathematical model is shown to be applicable for the zone melting process and can thus be applied to predict more reasonable parameters. Therefore, the computer simulations are advantageous and can arrange more efficient experiments.

5. Conclusions

Conventional phosphorus purification is an energy consuming and environmentally polluting process. This study proposes an efficient and zero pollution alternative for producing high purity phosphorus, the zone melting technique. According to the FDA and FCC standards, food grade phosphoric acid should have an arsenic concentration below 3 ppm for 85% phosphoric acid. Experimental results show that after the zone melting purification, the arsenic concentration in solid phosphorus is 10 ppm. The converted 85% phosphoric acid would have the arsenic concentration of 2.83 ppm only. Numerically, we have successfully simulated the zone melting process and obtained a better picture about the fusion time, the velocities of both interfaces, the length of the fusion region, and the shape of the melting zone. So far, we have only considered the heat conduction aspect of the zone melting process. In future theoretical modeling, the variation of the impurity concentrations during the zone melting process will be considered, which should provide more accurate guidelines to the zone purification experiments and make the mathematical model more complete.

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