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Research Article

Migration of Toxic Metals from Ceramic Food Packaging Materials into Acid Food Simulants

Zhanhua Dong,[1] Lixin Lu,[1,2] Zhigang Liu,[1,2] Yali Tang,[1,2] and Jun Wang[1,2]

[1] *Department of Packaging Engineering, Jiangnan University, Wuxi 214122, China*
[2] *Jiangsu Key Laboratory of Advanced Food Manufacturing Equipment and Technology, Wuxi 214122, China*

Correspondence should be addressed to Lixin Lu; lulx@jiangnan.edu.cn

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Long-term extraction experiments were carried out on glazed tile specimens with 4 and 10% (v/v) acetic acid, 1% (w/v) citric acid, and 1% (v/v) lactic acid solution in three temperature conditions (20, 40, and 60°C) to investigate the effect of temperature and pH value on extraction of lead, cobalt, nickel, and zinc from ceramic food packaging materials and to study the extraction kinetics of toxic metals. Results showed that except at 60°C the amount of extraction of lead, cobalt, nickel, and zinc had linear dependence on time at longer times and removal of these toxic metals under other conditions increased linearly with the square root of the time, indicating a diffusion-controlled process. The amount of these toxic metals leached out from ceramic food packaging materials into the leachate, and the leaching rate increased with temperature and decreased with pH value of the food simulants. In addition, among these four toxic metals lead was the least leachable element, and nickel was the most leachable one. Disagreement between the ratios of the oxide of lead, cobalt, nickel, and zinc in the glaze and their release in the leachate suggested that extraction of these toxic metals was an incongruent dissolution process.

1. Introduction

If ceramic food packaging containers which were widely used for storing a large variety of food substances such as mature vinegar, aromatic vinegar, and other more extractive acidic foodstuffs were decorated with the improperly formulated glazes and inappropriately fired, lead and other toxic metals would not be chemically combined closely in the glass structure [1], which will yield a high release of harmful toxic metals when contacting foodstuffs mentioned above and may even pose health hazards to the consumer.

The toxic properties of lead and cadmium are cumulative and systemic; even small amounts of them in continued daily intake will also lead to the damage of immune, reproductive, nervous, and other systems [2, 3]. Because of their acute toxicity, lead and cadmium have been considered as major risk for humans, and many steps have been taken to reduce or prevent their ingestion. In many countries, national legislation and international standards have been used by the authorities to monitor and regulate the possible release of lead and cadmium from all the potential sources [4–6].

Besides lead and cadmium, however, other toxic metals such as cobalt, nickel, and zinc were also detected in many kinds of glazed ceramic ware [7]. All these metals are trace elements essential to human body and generally considered to be relatively nontoxic, but long-term excessive intake will endanger human's health [8–10]. However, studies on their migration or extraction from ceramic wares into foodstuffs are rare and legislation or standards to monitor and regulate the possible release of these toxic metals are scarce. Therefore, it is necessary to study the leaching behavior of cobalt, nickel, and zinc from ceramic wares to evaluate their potential health hazards. Cadmium in ceramic glazes was also an important toxic metal of concern, which is under study now and will be discussed in detail elsewhere.

4% acetic acid solution was recognized as the most severe test solution for common beverages [11, 12], but many researches also reported that lead is removed with the increase of acid strength [13]. The pH value of 4% acetic acid is about 2.45, which is higher than that of 10% acetic acid (2.2). In addition, citric acid exists in all animal tissues and fluids, and lactic acid is primarily found in sour milk products and also found in various processed foods either as a pH adjusting ingredient or as a preservative [14], which are more significant for food ceramic packaging. In view of this, besides 4% acetic acid, 10% acetic acid, 1% citric acid (pH is about 2.21), and 1% lactic acid (pH is about 2.23) were also taken as test solutions for leaching lead and other toxic metals from ceramic food packaging containers in this study.

The present study aims at (1) investigating the extraction kinetics of lead, cobalt, nickel, and zinc from ceramic food packaging materials into acid food simulants; (2) inquiring into whether the ratio of the removal of these metals is coincident or not through the analysis of their amount in the leachate and their ratio in the glaze; (3) examining the effect of temperature on the extraction of these toxic metals; (4) studying the effect of the pH value of food simulants on extraction of these toxic metals.

2. Materials and Methods

2.1. Main Instruments and Reagents. The instruments used in this study included Lock&Lock (HPL812 1.1L) polypropylene airtight storage containers (Lock&Lock Co., Ltd., Korea), Perkin Elmer Optima 5100DV inductively coupled plasma optical emission spectroscopy (ICP-OES) (Perkin Elmer Corporation, USA), Milli-Q Element (Millipore Corporation, USA), THS-AOC-100 constant temperature humidity chamber (KSON Corporation, China), and PRX-450C Intelligent Artificial Climate Box (NoKi Corporation, China).

Reagents used in all tests of this study were of analytical grade at least.

The calibration curves were obtained by diluting 1000 mg/L standard stock solutions of lead (Pb), cobalt (Co), nickel (Ni), and zinc (Zn) (National Research Center for Certified Reference Materials, China; NRCCRM) with the acid food simulants mentioned above. The working standards of final concentrations for lead, cobalt, nickel, and zinc were 0.0, 0.2, 1.0, 2.0, 10.0, 20.0, and 100.0 μg/mL, respectively.

2.2. Preparation of Specimens. A number of ceramic specimens with an average of $11.15 \times 5.62 \times 0.73\,\mathrm{cm}^3$ in volume were collected from the same lot from a ceramic company in Yixing, Jiangsu, China. Ceramic specimens were fired at a low temperature (about 850°C) in a muffle furnace, glazed with a glaze whose composition is K_2O 1.89%, Na_2O 0.88%, ZnO 6.07%, PbO 41.47%, Fe_2O_3 0.07%, CoO 4.04%, NiO 4.04%, MgO 0.05%, CaO 0.13%, Al_2O_3 6.69%, and SiO_2 34.67%, and fired a second time at 1120°C after they were dry, and the glaze would be fused onto the surface of clay tiles forming a thin layer of glass.

Ceramic specimens were prepared according to the method of ASTM C 738-94(2006) [4], washed with detergent, rinsed with tap water followed with deionized water, and then taken out from an electrically heated drying cabinet after they were dry.

2.3. Experiment Design. Experiment was designed to study the effects of temperature and pH value on extraction of lead, cobalt, nickel, and zinc from food packaging materials and to examine the extraction kinetics of these four toxic metals into the acid food simulants mentioned above at temperatures 20, 40, and 60°C. Five tile specimens were placed in a Lock&Lock polypropylene airtight storage container at the constant temperature box whose temperature was designated for 2 hours and its temperature stability was better than ±0.1°C. After the tile specimens reached equilibrium with the temperature of the constant temperature box, 450 mL of food simulants which were prepared to the designated temperature was added into the Lock&Lock polypropylene airtight storage container. The temperature was set at 20, 40, and 60°C. Leaching tests were continued for 720, 800, and 600 h, respectively. During the extraction experiments, 2 ± 0.1 mL of leachate was periodically transferred into a PP centrifuge tube with a pipette for storage before measuring lead, cobalt, nickel, and zinc concentrations using inductively coupled plasma optical emission spectroscopy (ICP-OES); then the volumes of the prepared food simulants were made up to the initial values in order to compensate for evaporation losses and keep a constant pH value. In all experiments, each test was repeated five times.

2.4. Concentration Correction. Because of the loss of toxic metals in the extraction liquid resulting from periodically sampling, concentrations of lead, cobalt, nickel, and zinc should be corrected to ensure the accuracy of values which we used. The concentrations of lead, cobalt, nickel, and zinc were corrected using an equation as follows:

$$y_j = x_j + \frac{2}{450} x_{j-1} \quad (y_1 = x_1;\ j = 2, 3, 4, \dots, n), \tag{1}$$

where y_j is the concentration corrected and x_j is the measured value. Volume of food simulants used in one Lock& Lock polypropylene airtight storage container is 450 mL, and the sampling volume is 2 mL.

3. Results and Discussion

To ensure the uniformity and allow the intercomparison of the results, concentrations of lead, cobalt, nickel, and zinc extracted with 4 and 10% acetic acid, 1% citric acid, and 1% lactic acid at 20, 40, and 60°C were converted to a normalized mass loss in μg/cm^2 according to

$$\mathrm{NM}_i = \frac{C_i * V}{S}, \tag{2}$$

where NM_i (μg/cm^2) is the normalized mass loss of element i (lead, cobalt, nickel, and zinc), C_i (μg/mL) represents the concentration of element i in the leachate measured by ICP-OES, V (mL) is the volume of food simulants used in the tests, and S (cm^2) is the area of the tile specimen. Each data was the average value of the amount determined from five tests.

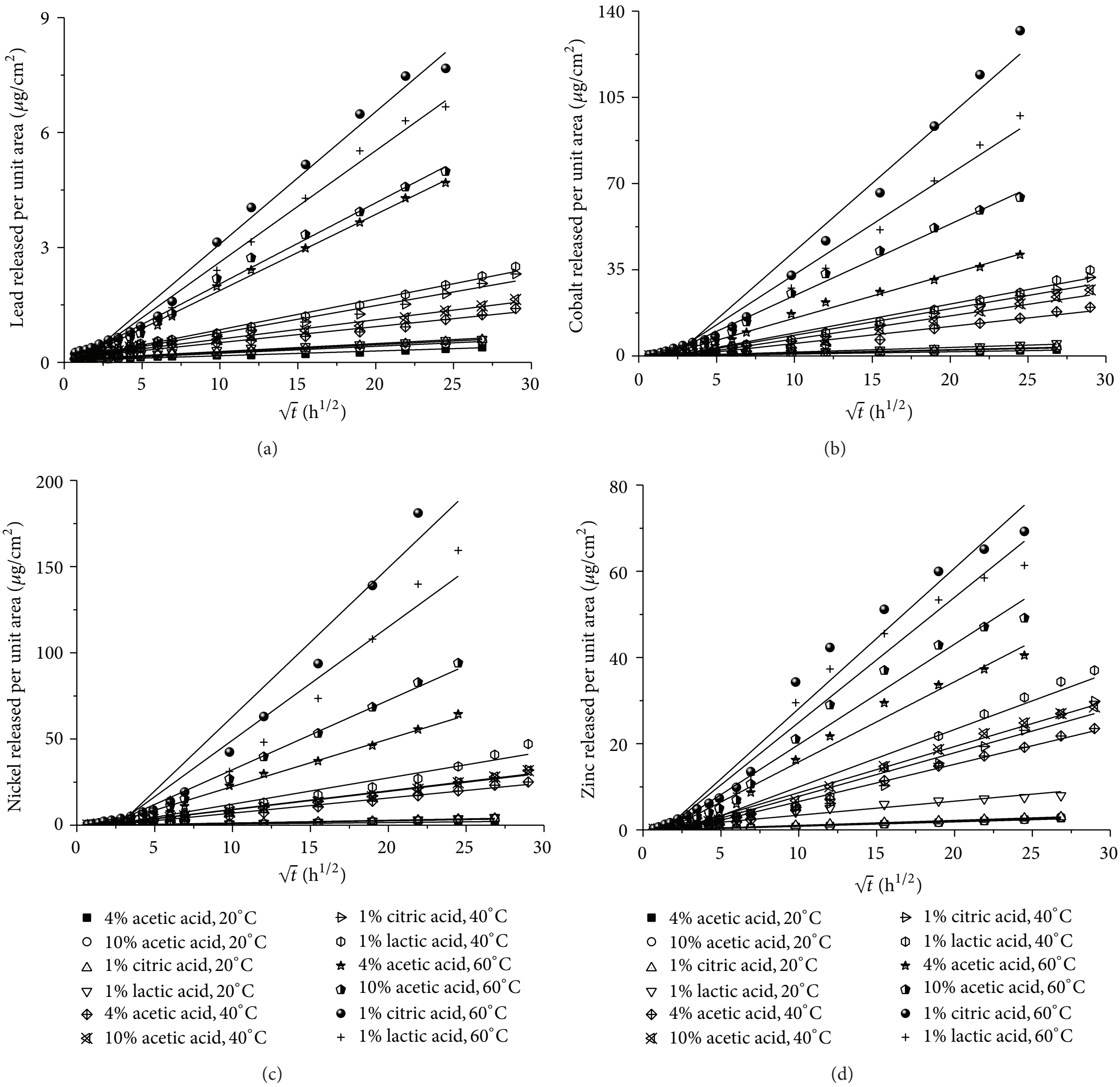

FIGURE 1: Amount of lead, cobalt, nickel, and zinc released by acid food simulants at 20, 40, and 60°C as a function of $t^{1/2}$: (a) lead, (b) cobalt, (c) nickel, and (d) zinc.

3.1. Kinetics of the Migration of Lead, Cobalt, Nickel, and Zinc. Figure 1 illustrated the results of extraction of lead, cobalt, nickel, and zinc from food packaging materials into acid food simulants under all conditions. In order to study the kinetics of the extraction, linear regression analyses were performed on all leaching data for lead, cobalt, nickel, and zinc removal from the beginning of the contact till the end of the experiment, and several plots of the amount of lead, cobalt, nickel, and zinc released per unit area against the square root of the time were made. The formula of Linear Fit is given by

$$\mathrm{NM}_i = a + b \times \sqrt{t}, \tag{3}$$

where NM_i is the normalized mass loss of element i, a and b are the parameters obtained by calculating the leaching data of the experiment, and t is the contact time.

From Figure 1, it was apparent that the amount of lead, cobalt, nickel, and zinc released from the ceramic food packaging material by 4 and 10% acetic acid, 1% citric acid, and 1% lactic acid at 20 and 40°C all increased linearly with the square root of the time. The square of correlation coefficient (R^2) of the extraction data and Linear Fit straight line were all above 0.95, indicating that the extraction of these toxic metals by acid food simulants at 20 and 40°C was a diffusion-controlled process, which has been reported by many researchers [15–17].

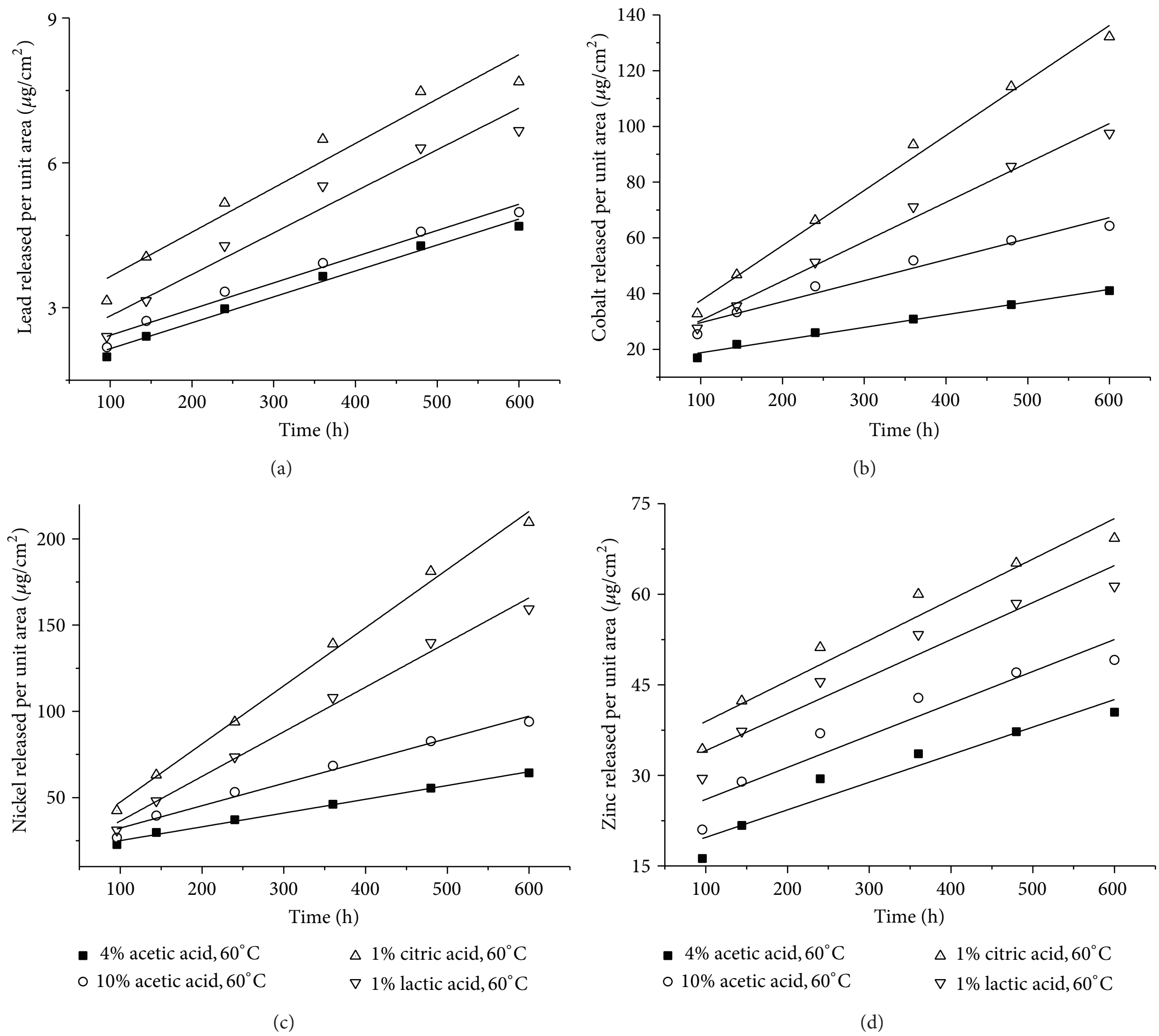

FIGURE 2: Amount of lead, cobalt, nickel, and zinc released by acid food simulants at 60°C as a function of time: (a) lead, (b) cobalt, (c) nickel, and (d) zinc.

However, there was a notable exception for extraction of lead, cobalt, nickel, and zinc with acid food simulants at 60°C, with perhaps a change to a linear dependence with time at longer times; for example, $t > 100$ h, as shown in Figure 2. This phenomenon agrees well with the study of Seth et al. [18] and Douglas and EL-Shamy [19], who reported that the amount of lead was varied as $t^{1/2}$ at short times and low temperatures and directly as the time at long times and high temperatures. The change from root time dependence to linear dependence on time could be the result of the change of leaching or extraction mechanism when temperature goes up to 60°C. When temperatures were at 20 and 40°C, lead, cobalt, nickel, and zinc leached via ion exchange controlled by interdiffusion of cations such as Pb^{2+}, Co^{2+}, and H_3O^+ through the structure of the ceramic food packaging materials. However, when temperature goes up to 60°C, migration of lead, cobalt, nickel, and zinc could be affected by the dissolution of the network of ceramic food packaging materials. This phenomenon agrees well with the study of Seth et al. [18] and Douglas and EL-Shamy [19], who reported that the amount of lead varied as $t^{1/2}$ at short times and low temperatures and directly as the time at long times and high temperatures. In addition, Wood and Blachere [20] also observed a change from square root of time dependence of the amount of lead extracted from the 65-35 lead silicate glass to a linear dependence with time at longer times and higher temperature (e.g., $t = 200$ h at 50°C). We ascribed this phenomenon to the change of the migration mechanism of lead, cobalt, nickel, and zinc. When temperature is higher than 60°C, the migration mechanism can be changed from ion exchange to network dissolution or hydrolysis which was controlled by surface reaction whose characteristic is time dependence. Ojovan et al. [21] also reported that the mechanism of glass corrosion could be changed quickly

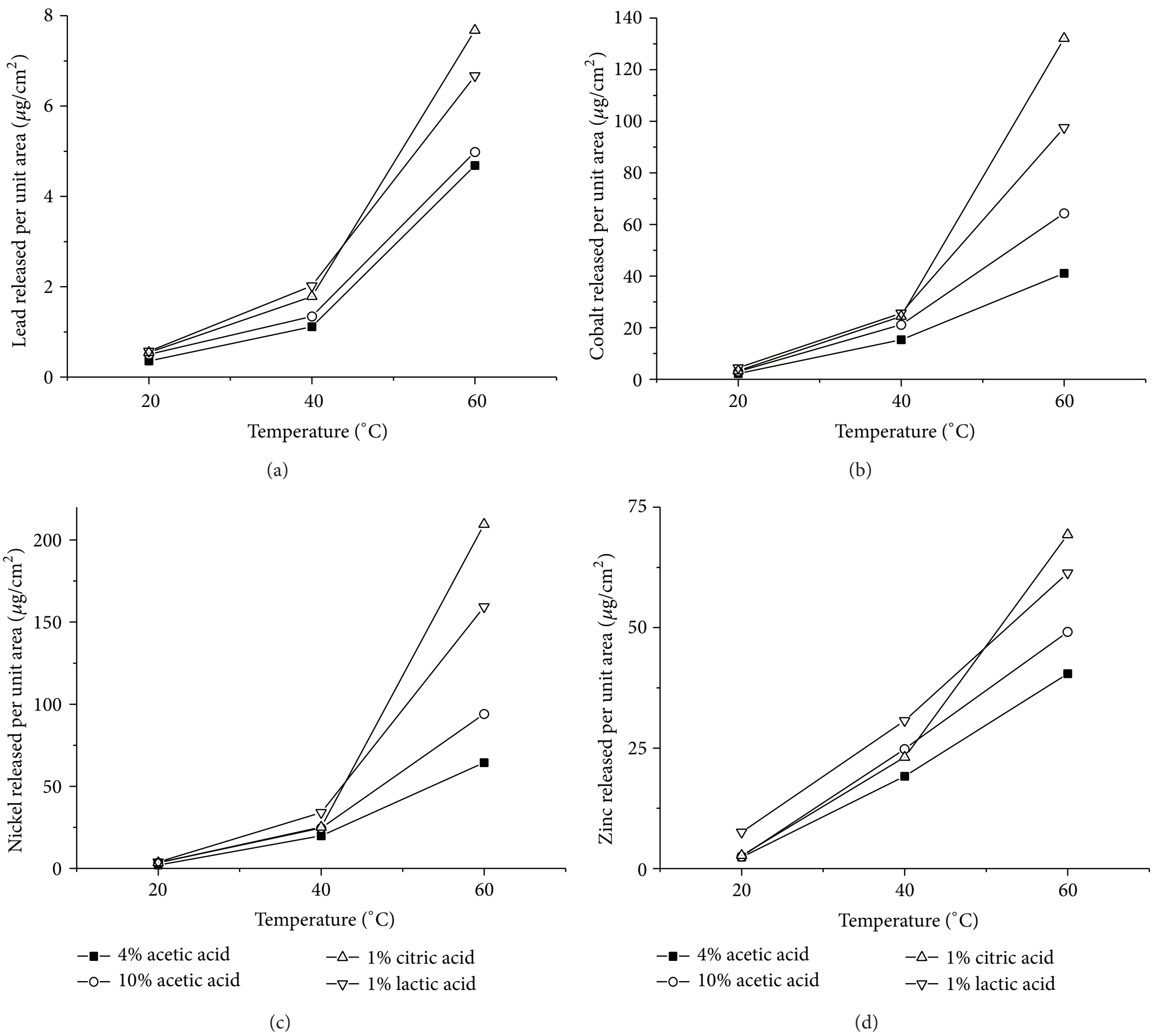

Figure 3: Effect of temperature on extraction of lead, cobalt, nickel, and zinc by 4 and 10% acetic acid, 1% citric acid, and 1% lactic acid at 20, 40, and 60°C: (a) lead released per unit area at 600 h, (b) cobalt released per unit area at 600 h, (c) nickel released per unit area at 600 h, and (d) zinc released per unit area at 600 h.

from ion exchange to hydrolysis at high temperatures, and transition times could span from hours to several days.

3.2. Effect of Temperature on Migration of Lead, Cobalt, Nickel, and Zinc. In Figure 3, data points in (a), (b), (c), and (d) represent the amount of lead, cobalt, nickel, and zinc released per unit area at 600 h at 20, 40, and 60°C, respectively. It can be seen clearly that the extraction of lead, cobalt, nickel, and zinc from the ceramic specimens all increased with temperature, which could be the result of lower diffusion activation energy and higher diffusion coefficient caused by high temperature that makes the ion exchange reactions occur more rapidly, and hence the extraction of these toxic metals occurs more easily. Through the comparison of the slope of the straight lines formed by the amount of lead, cobalt, nickel, and zinc released with each food simulant at three temperatures, such a phenomenon can be obtained: the rates of removal of toxic metals also increase with temperature, and the biggest effect of temperature exists in nickel release in 1% citric acid and the least one in zinc release in 10% acetic acid.

3.3. Relationship between the Amount of Toxic Metals Released and the Ratio of Their Oxides in the Glaze. Relationship between the amount of toxic metals released and the ratio of their oxides in the glaze can also be obtained from the experiment of the effect of temperature on extraction. In Figure 3, it was clearly depicted that food packaging ceramic specimens yielded the least amount of lead under all test conditions, and the amount of cobalt, nickel, and zinc

Table 1: Lead : cobalt : nickel : zinc mass ratios in leachate and in glaze.

Food simulants	Temperature	Pb : Co : Ni : Zn Leachate	Pb : Co : Ni : Zn Glaze
4% acetic acid	20	1 : 6.24 : 5.72 : 6.74	1 : 0.097 : 0.097 : 0.146
	40	1 : 13.75 : 17.81 : 17.15	
	60	1 : 8.76 : 13.73 : 8.63	
10% acetic acid	20	1 : 6.09 : 6.82 : 4.97	
	40	1 : 15.72 : 17.81 : 17.15	
	60	1 : 12.91 : 18.87 : 9.86	
1% citric acid	20	1 : 6.11 : 6.40 : 5.04	
	40	1 : 13.69 : 14.10 : 12.94	
	60	1 : 17.22 : 27.30 : 9.03	
1% lactic acid	20	1 : 7.69 : 6.98 : 13.19	
	40	1 : 12.71 : 16.88 : 15.23	
	60	1 : 14.62 : 23.89 : 9.20	

are much more than lead. This phenomenon can also be described clearly by lead : cobalt : nickel : zinc mass ratios in leachate at 600 h and that in glaze in Table 1.

The ratios of the oxide of these toxic metals in the glaze were 1 : 0.097 : 0.097 : 0.146 (PbO 41.47 wt%, CoO 4.04 wt%, NiO 4.04 wt%, and ZnO 6.07 wt%). It was obvious to see that lead content is the highest one of all four heavy metals in glaze and up to 41.47%; however, the migration amount of lead in leachate is the lowest one. In glaze, the contents of cobalt and nickel are equal to 4.04 wt% and are much less than that of lead in glaze, but the migration amount of nickel is almost the highest one among these four metals and is much more than that of lead. The migration amount of cobalt in leachate is a little lower than that of nickel. The content of zinc in glaze is 6.07 wt%, which is a little higher than that of cobalt and nickel but much less than that of lead. The migration amount of zinc is less than migration amount of nickel and cobalt but is still more than that of lead in leachate. Disagreement between the ratios of the oxide of these toxic metals in the glaze and their release in the leachate suggested that nickel was most easy to release, followed by cobalt and then zinc, and lead was the least. This also indicated the incongruent release process of toxic metals from the glaze when ceramic materials contacted acid food.

3.4. Effect of pH Values on Migration of Lead, Cobalt, Nickel, and Zinc. Although citric acid, lactic acid, and acetic acid all exist in natural food and the pH values of 1% citric acid, 1%lactic acid, and 10% acetic acid are about the same, the nature of citric acid, lactic acid, and acetic acid is different, especially citric acid that is tricarboxylic acid, which could form tridentate complexes with the heavy metals in glaze, hence leading to a high migration level. Therefore, we chose 4 and 10% acetic acid to study the effect of pH value on migration of lead, cobalt, nickel, and zinc. Through the comparison of all the data of 4 and 10% acetic acid leaching test, it can be found that the normalized amounts of toxic metals in 10% acetic acid are more than those in 4% acetic acid, which can be seen from the comparison of data points in Figure 3, in which black solid square data points denote the amount of toxic metals extracted by 4% acetic acid and hollow circle data points denote the amount of toxic metals extracted by 10% acetic acid. This phenomenon indicated that 10% acetic acid was more effective in extractability of lead, cobalt, nickel, and zinc, which could be the effect of a lower pH value of 10% acetic acid than that of 4% acetic acid (pH value of 4% acetic acid is about 2.45 and that of 10% acetic acid is about 2.2). Yoon et al. [22] reported that lead release decreased linearly with the increase of pH value under a certain temperature. Sheets and Turpen [13] also concluded that leached lead increased with the increase of acid strength. However, such extreme acidic conditions (10% acetic acid) are unlikely to occur for foodstuffs. Therefore, the EU and FDA test use 4% acetic acid, which is much closer to the real situation, to extract toxic metals of ceramic wares.

4. Conclusion

The amount of lead, cobalt, nickel, and zinc released into all the four kinds of food simulants at 20 and 40°C varied linearly with the square root of time which indicated a diffusion-controlled process that occurred in the contact between the glaze and food simulants. Exception for the extraction kinetics of linear dependence of time at 60°C revealed a change of extraction mechanism from ion exchange to network dissolution. Extraction of these four toxic metals into the food simulants and extraction rate increased with the temperature and decreased with the pH value. Disagreement between the ratios of the oxide of these toxic metals in the glaze and their release into the food simulants suggested that dissolution of glaze was not a congruent process.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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